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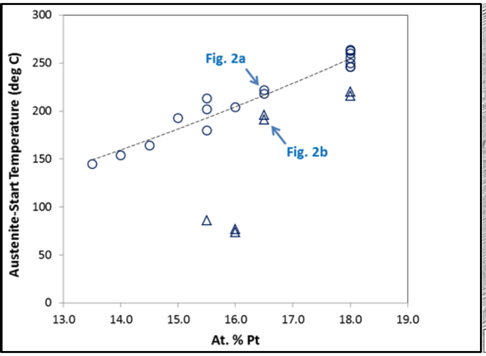

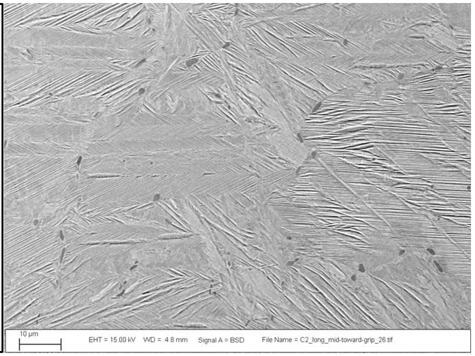

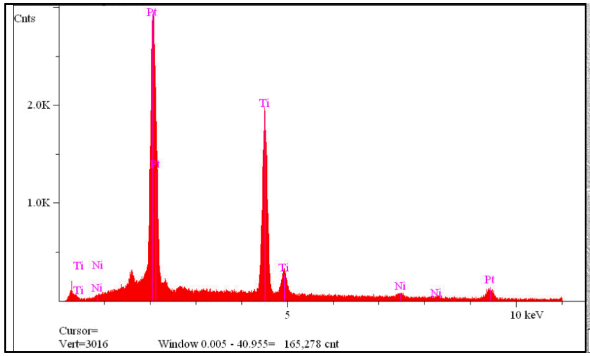

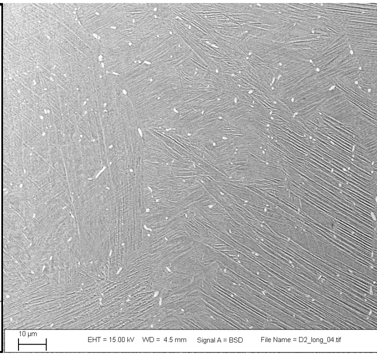

Confirming the Composition of Shape Memory Alloys by Microstructural Characterization

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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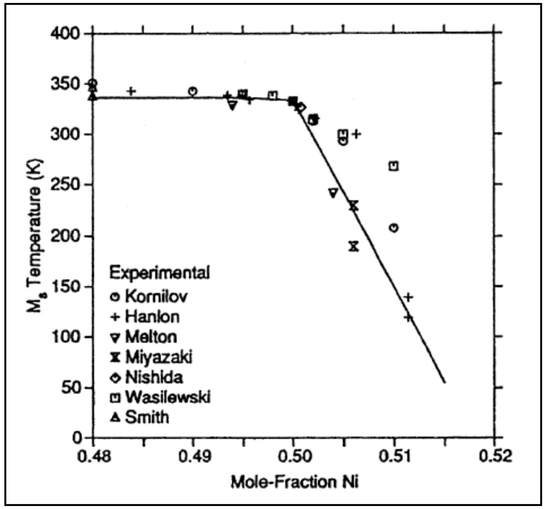
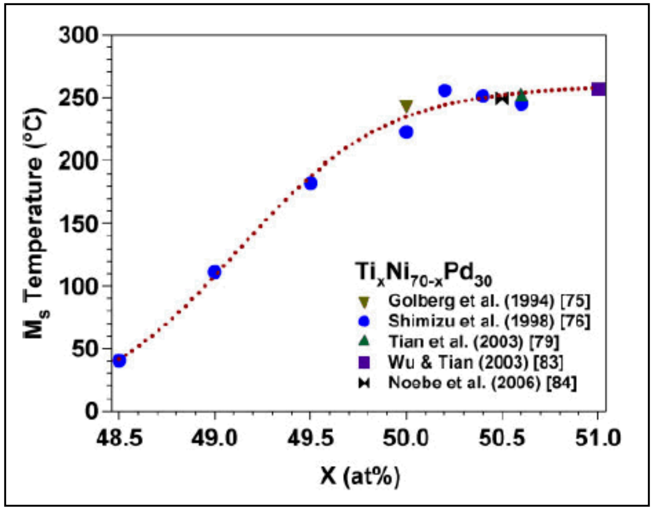
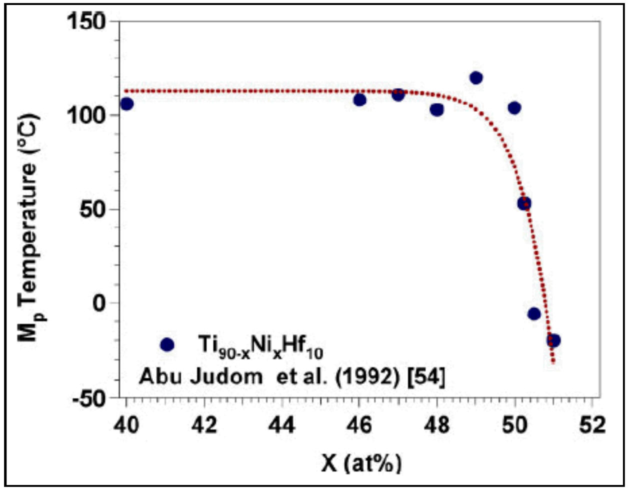
Overview

- The properties of shape memory alloys (SMA), such as binary Ni-Ti or ternary Ni-Ti-X alloys, are sensitive to composition
- Temperatures of phase transformation from martensite to austenite or vice-versa can be greatly affected by composition changes of tenths of wt.%
  - Examples Ni-Ti, Ni-Ti-Pd (Pd substituting for Ni), Ni-Ti-Hf (Hf substituting for Ti) shown below
  - This presentation: Ni-Ti-Pt (Pt substituting for Ni) alloys, in which we would expect similar effects







← More Ni-rich

More Ni-rich →

K. Otsuka and X. Ren, *Prog. Mat. Sci.*, Vol. 50, 511-678, 2005

J. Ma, I. Karaman, and R. Noebe, *Int. Mat. Rev.*, Vol. 55, 257-315, 2010

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SMA Behavior Related to Phase Diagram, Ni-Rich vs. Ti-Rich Stoichiometry

Ti-rich alloys generally do not undergo precipitation reactions

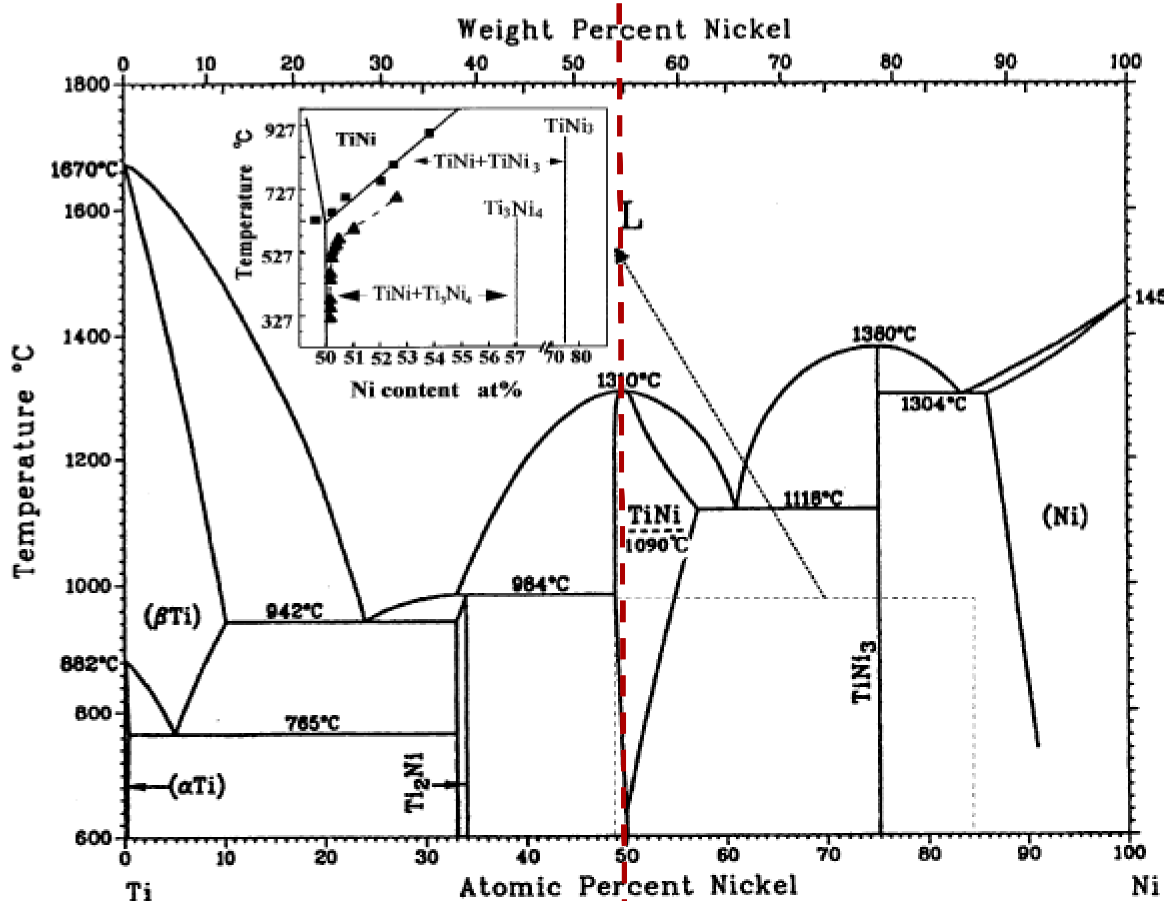


Fig. 2. Phase diagram of a Ti–Ni alloy by Massalski [55], to which the phase equilibrium between the B2 and Ti_3Ni_4 phases are added [56] (reproduced with the permission of ASM International and Materials Research Society). (K. Otsuka and X. Ren, *Prog. Mat. Sci.*, Vol. 50, 511-678, 2005)

Ni-rich alloys can be heat treated to induce precipitation (age hardening) reactions

Ti_2Ni_3, Ti_3Ni_4, depending on time and temperature, "P-phase" etc.

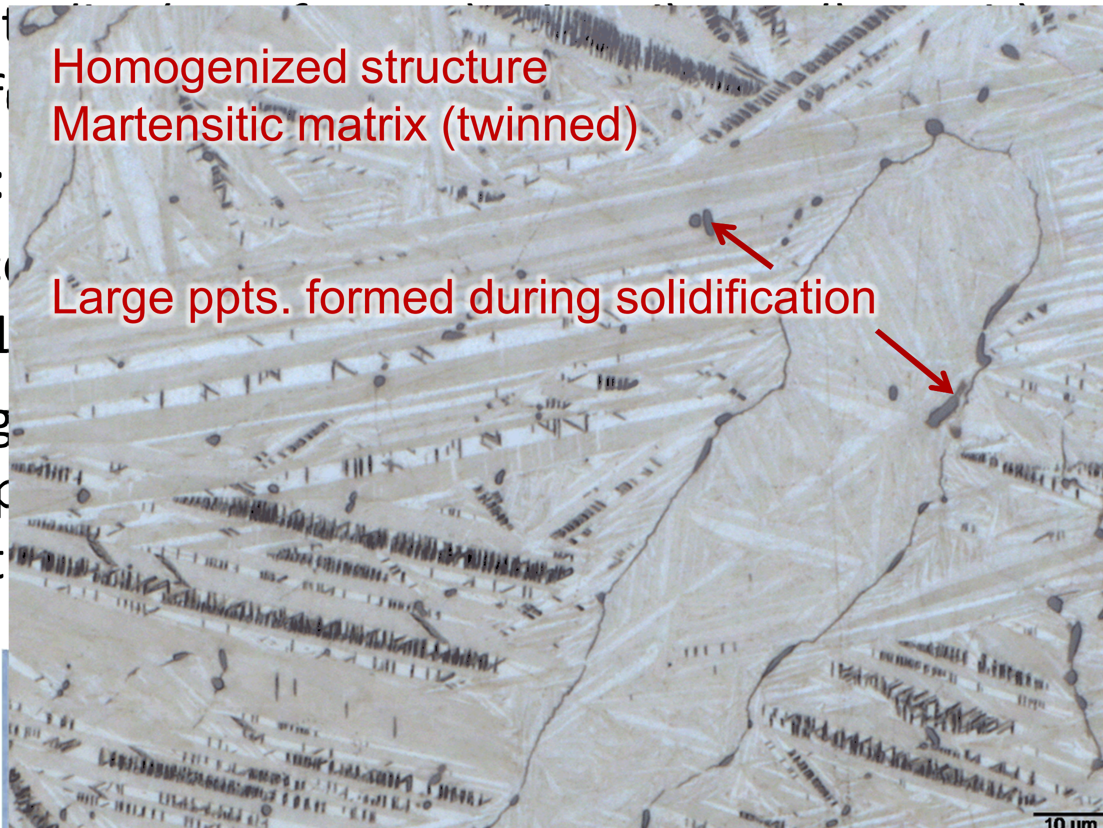
TEM required to confirm

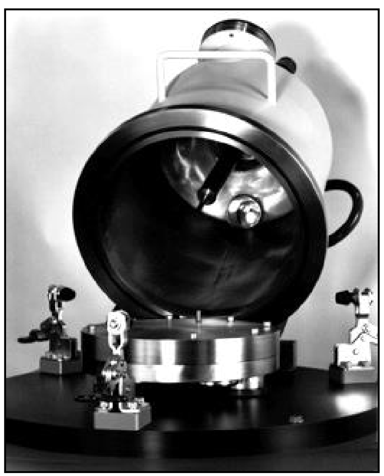
Role of Stoichiometry in Controlling Behavior of SMAs (not just Transf. Temps.)

- **Ti-rich or Ti(Hf)-rich alloys**
  - **Higher transformation temperatures**
    - **Reason for primary emphasis on ternary systems**
  - **No control over microstructure (contain Ti_2Ni ($Ti_4Ni_2O_x$) particles from melting)**
  - **Actuator properties (load-biased thermal cycling response):**
    - **Often greater transformation (recoverable) strain**
    - **Always Poor dimensional stability**
    - **TWSME**
- **Ni-rich or Ni(Pt,Pd)-rich alloys**
  - **Lower transformation temperatures (but they can be recovered by aging)**
  - **Microstructural control – many options –Ni_4Ti_3, P-phase, Orthorhombic, & other phases**
  - **Actuator properties**
    - **Smaller transformation strain**
    - **Outstanding dimensional stability**
  - **Good superelastic properties**

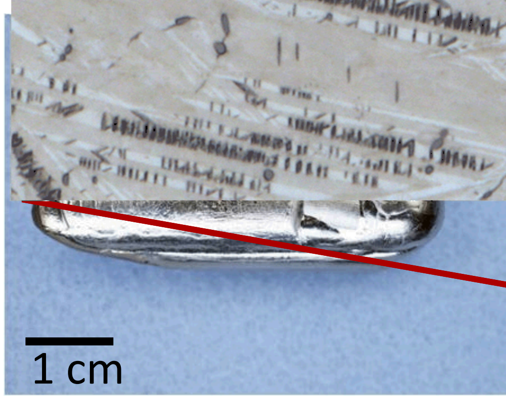
Ternary Ni-Ti-Pt Alloys

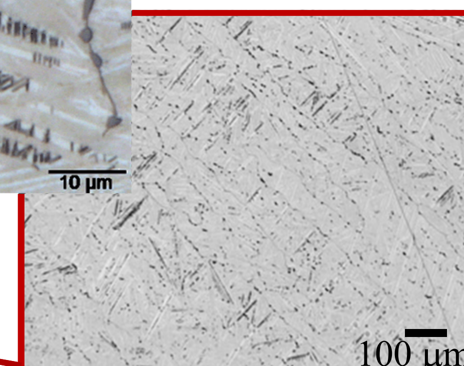
- Previous st … 20 at.% Pt and transf …
- This work: … 0-250˚C
- “Target” c … s of ingots between 1 …
- Processing … to ensure macroscop … at treatment …





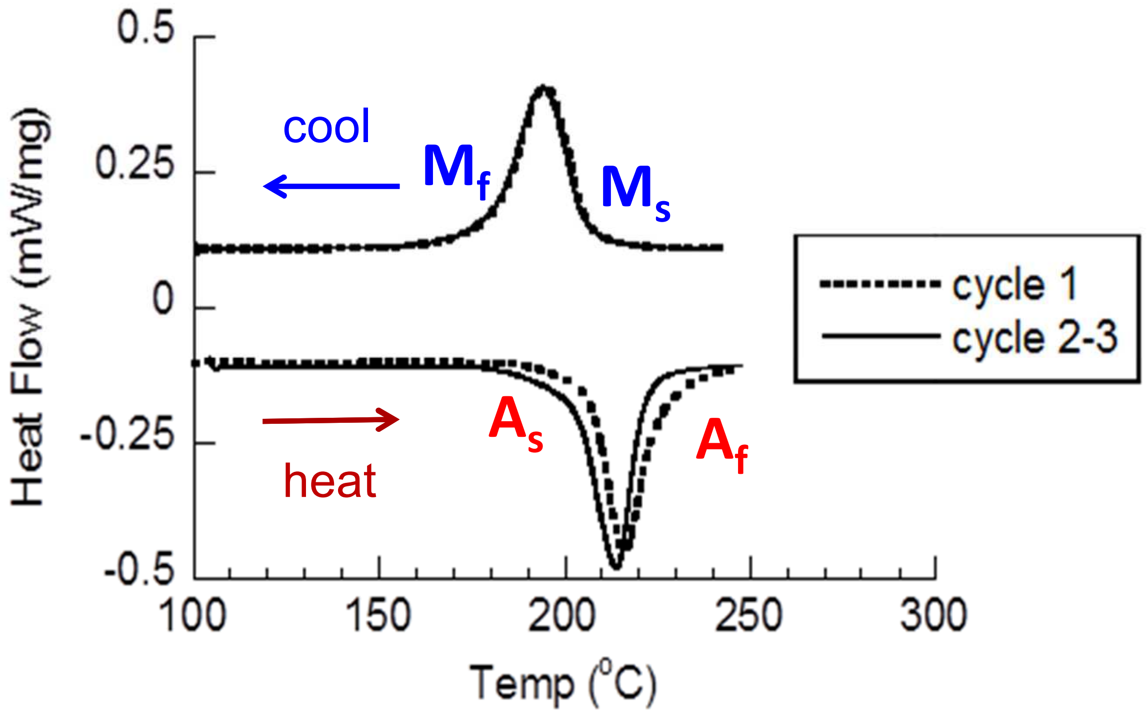
Arc button melter





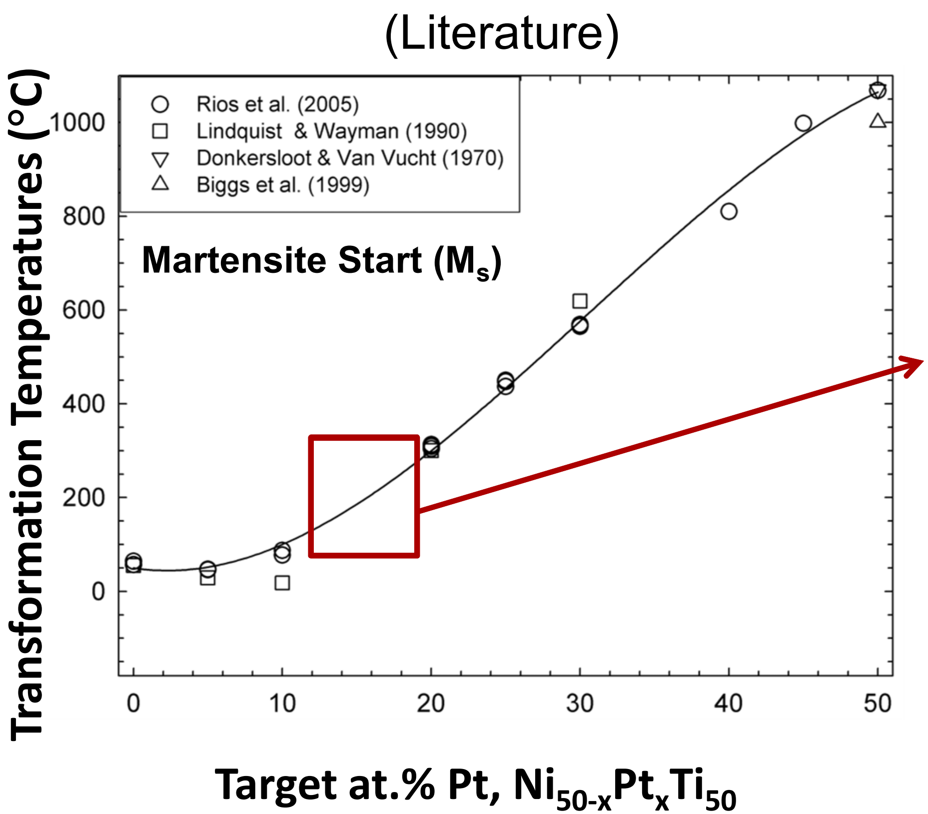
Optical Metallography

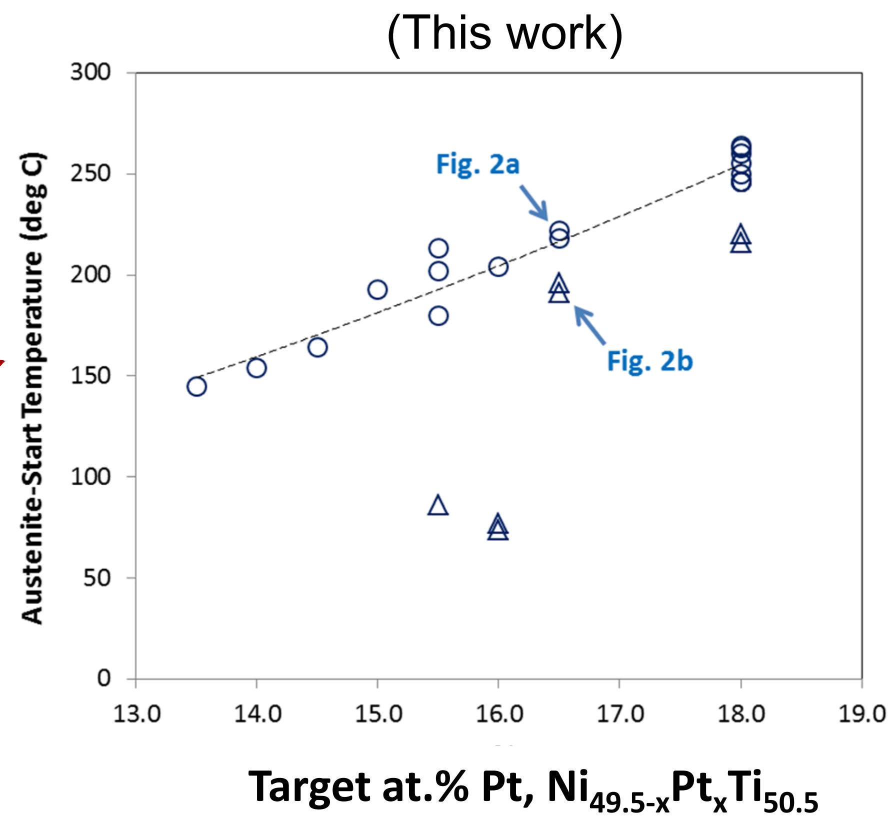
Phase Transformation Temperatures Determined by Differential Scanning Calorimetry (DSC)



- Austenite start and finish on heating, Martensite start and finish on cooling
- Ramp rate 10˚C/min, DSC traces stabilize in 2-3 thermal cycles
- DSC results give an *indirect* indication of chemistry of a given ingot, microstructural characterization is needed to *confirm*. (Bulk chemical analysis methods: too much uncertainty to determine the very small differences in composition we are trying to measure.)

Ternary Ni-Ti-Pt Alloys Produced in this Study

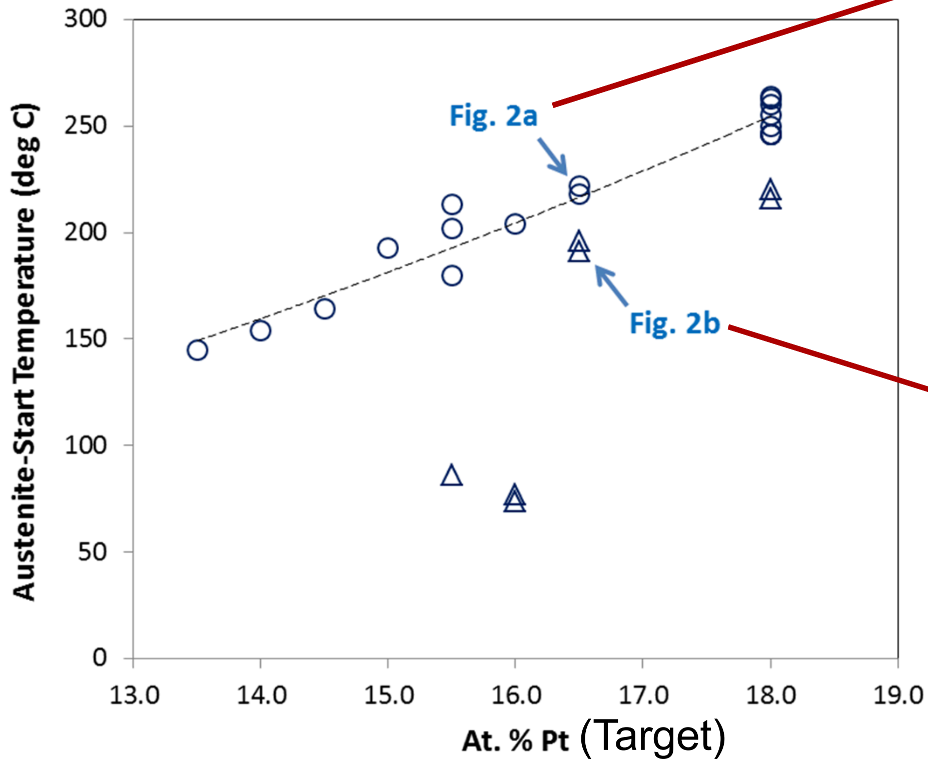


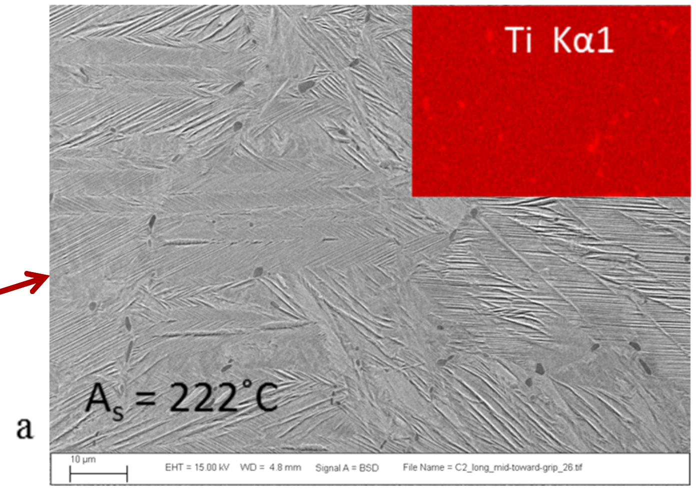


150-250 °C Transformation Temperatures = New Range of Compositions

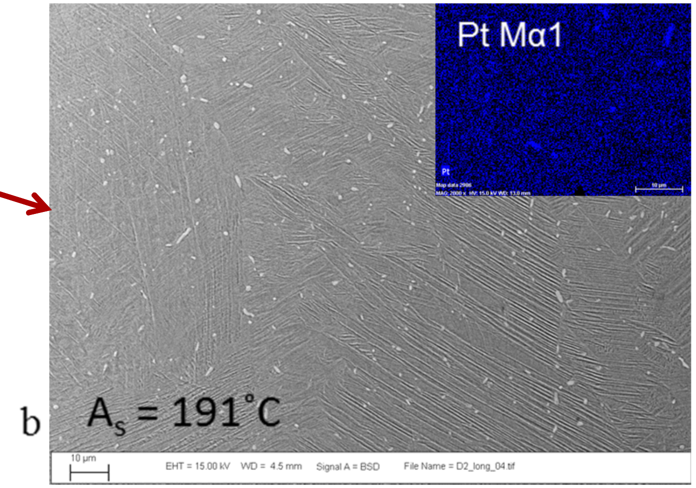
Scanning Electron Microscopy and Energy Dispersive Spectroscopy (EDS) Elemental Maps

- Unexpected differences in the types of precipitates observed – another indication of possible Ni-rich composition.
- Very slight changes in chemistry can occur due to: Ti oxidation, inhomogeneity during melt processing, etc.





Ti-rich ($Ti_2(Ni,Pt)$) ppts., supports Ti-rich chemistry



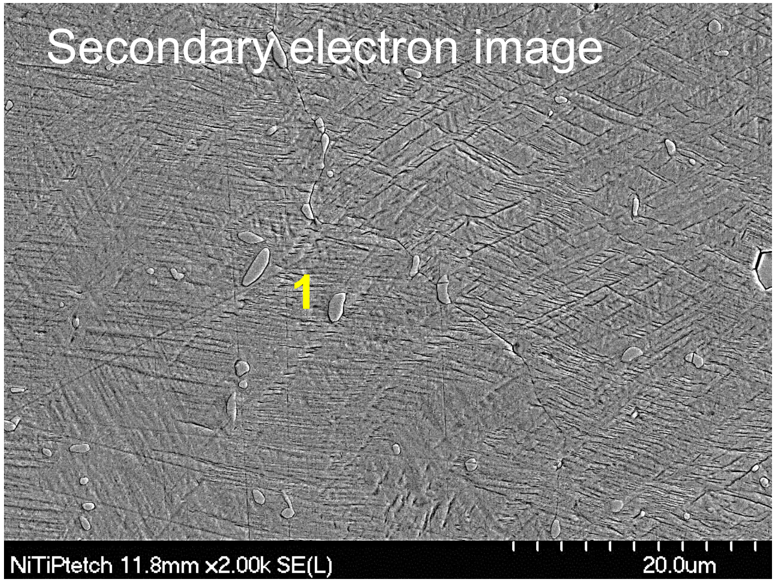
(Ni,Pt)-rich ppts., indicate Ni-rich alloy

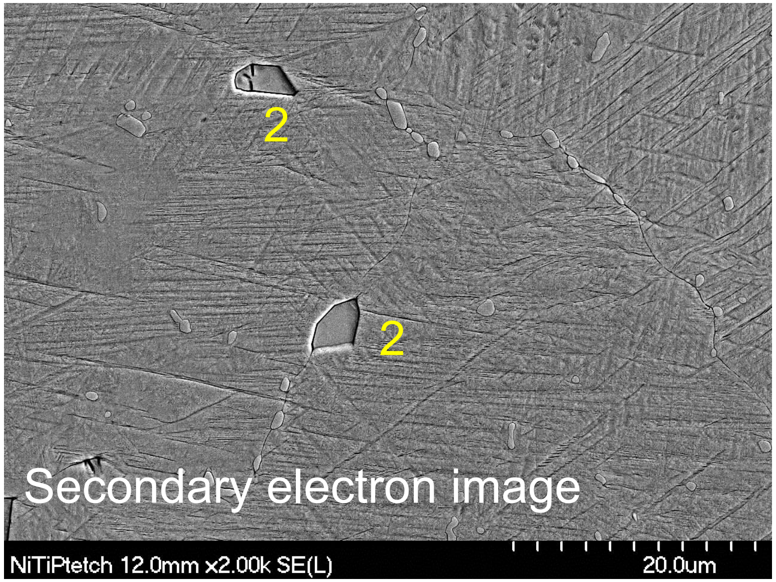
SEM/EDS on Micron-Sized Precipitates

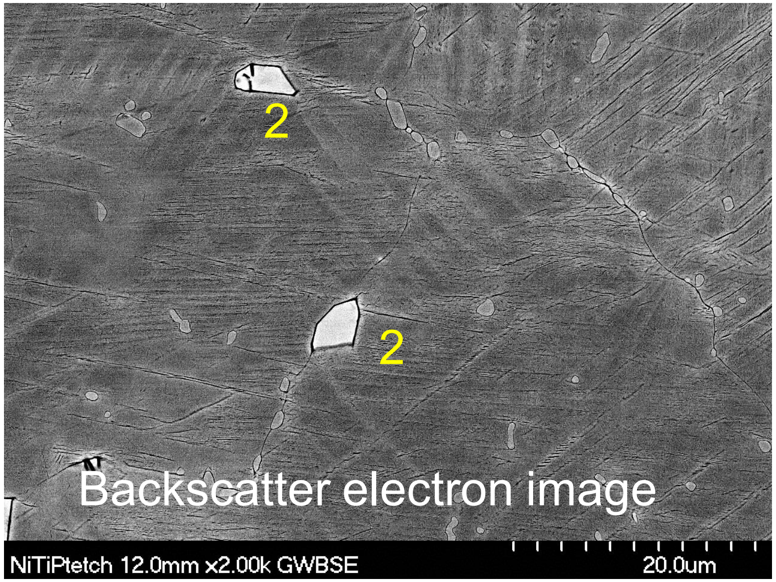
- Ni-Ti-16.5 at.% Pt target composition
- Homogenized 60 hrs., 1050 deg C
- Two types of micron-sized precipitates

Semi-Quant EDS analysis in at. %

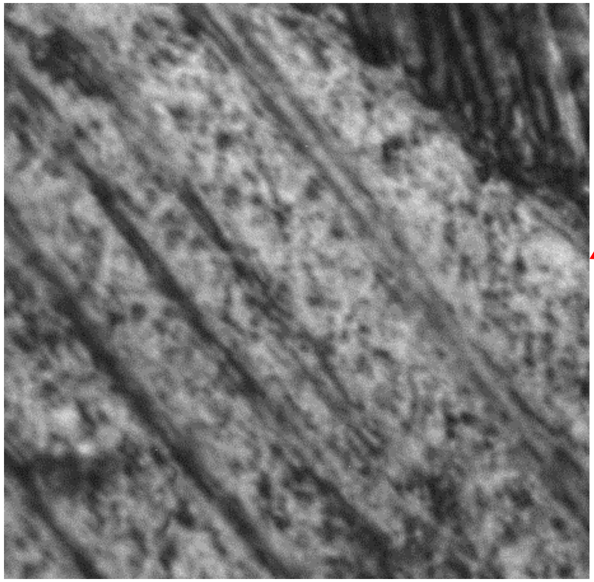
	Ni	Ti	Pt
Particle 1	4	64	32, likely $Ti_2(Pt,Ni)/Ti_4(Pt,Ni)_2O_x$
(oxide stabilized phase, forms during melt processing)			
Particle 2	14	48	38, possibly Pt-rich (Pt,Ni)Ti
Matrix	31	47	22, (Ni,Pt)Ti



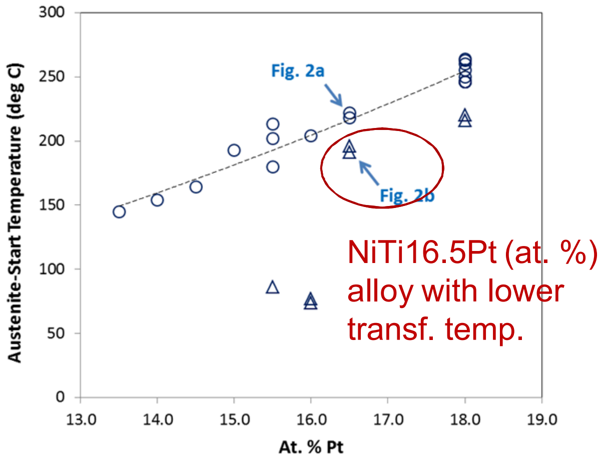




TEM: Precipitation of nm-size Second Phase

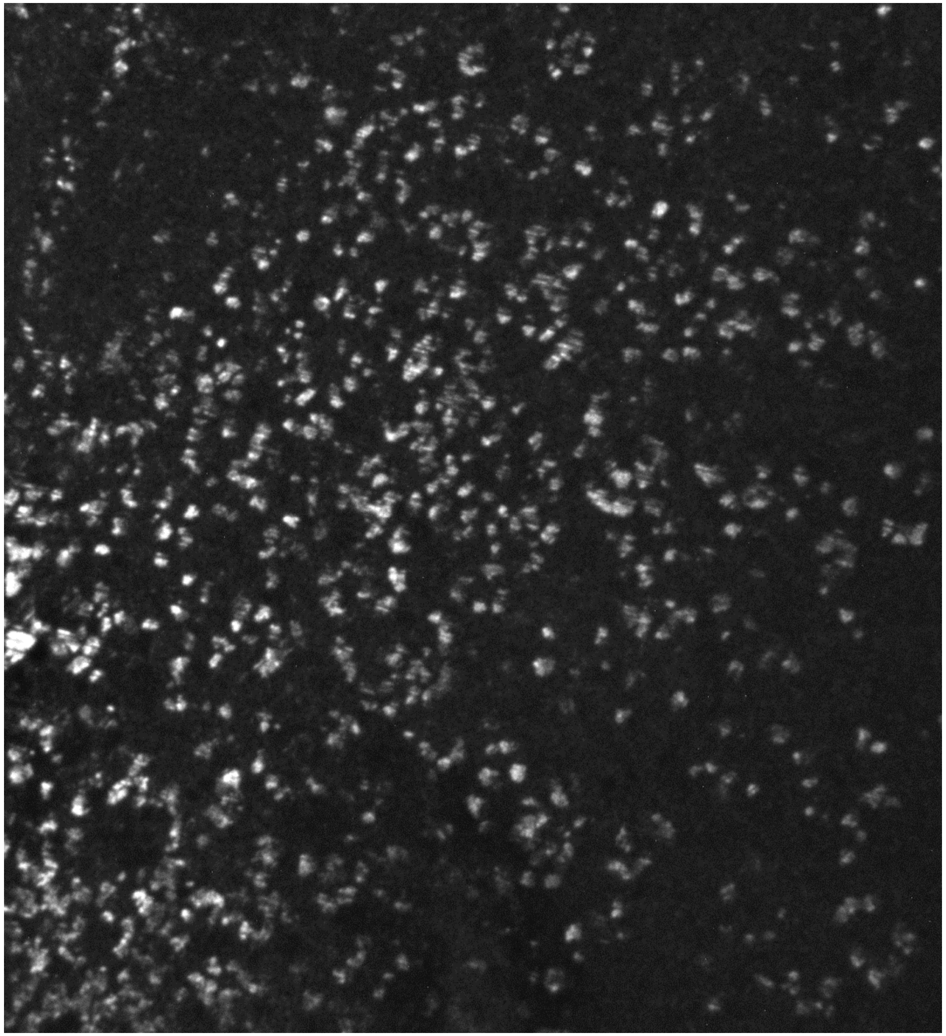


Fine precipitates $\leq 10\text{nm}$

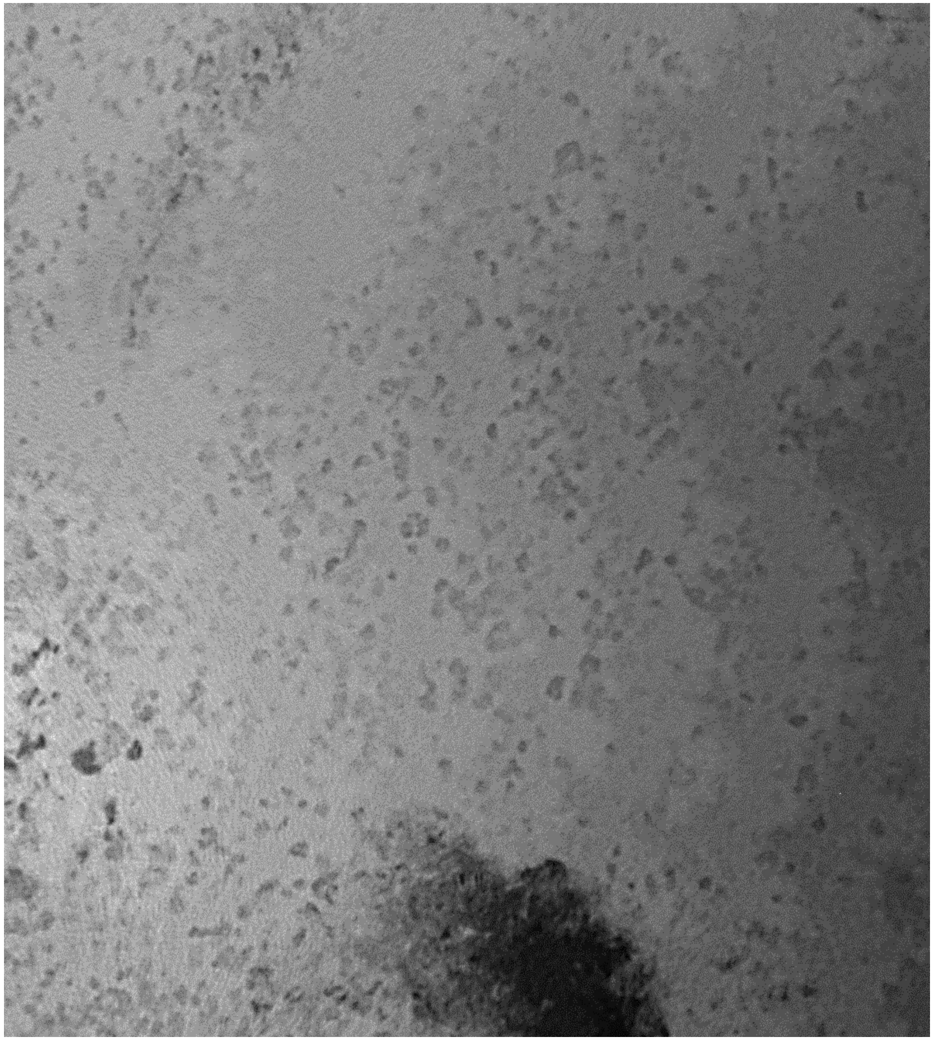


General microstructure showing martensite laths and very fine ppt. phase at room temperature

TEM of Fine Precipitates



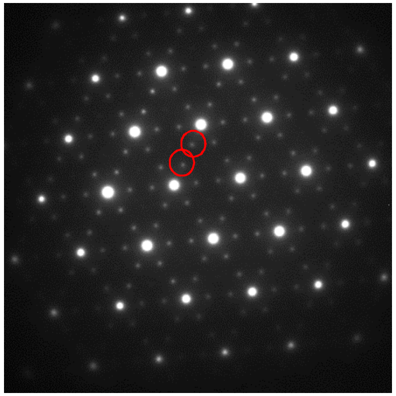
Dark-Field TEM image



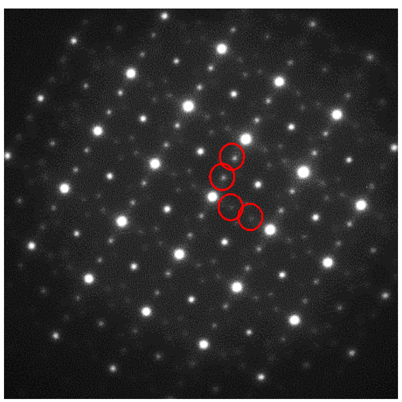
Corresponding Bright-Field TEM image

Diffraction Analysis

ZA: <111>B2

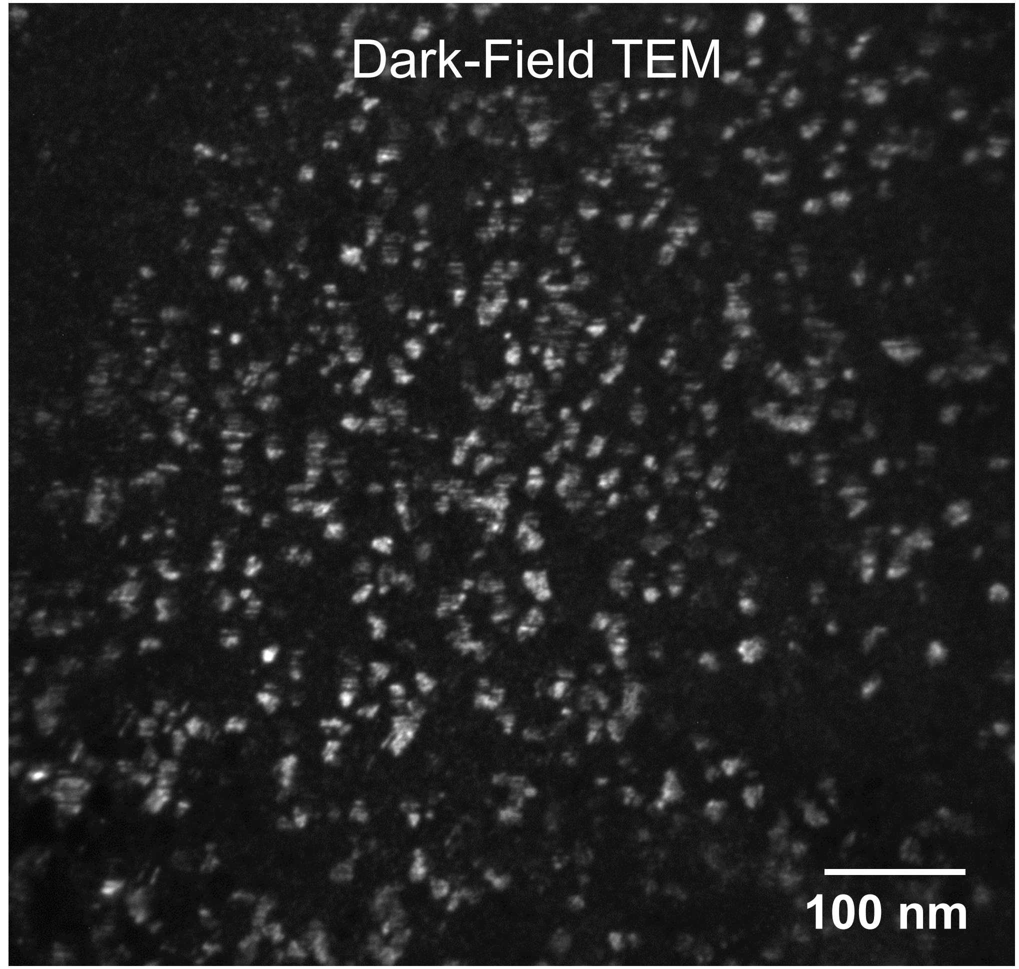


ZA: <100>B2



Diffraction patterns showing characteristic “P-phase*” ppt. spots (circled in red)

P-phase is monoclinic Ni9Pt4Ti11



Presence of fine ppts. suggests that the alloy is Ni-Rich.

* Acta Materialia (58) 2010, 4660-4673.

Summary

- The properties of binary NiTi and ternary Ni-Ti-X shape memory alloys are sensitive to composition, especially on the Ni-rich side of stoichiometry.
- A range of NiTiPt alloys were produced with 13-18 at.% Pt, with target composition slightly Ti-rich (50.5 at.% Ti).
- DSC results indicate generally good agreement with expected trend of transformation temp. vs. Pt content. However, a few ingots showed low transf. temps. relative to the trend line.
- SEM and TEM characterization are required to determine whether fine-scale precipitates exist. The presence of fine-scale precipitates, such as P-phase, confirms that the alloy composition is Ni-rich. The microstructural characterization corroborates well with (indirect) DSC data.