In Situ Neutron and Synchrotron X-ray Diffraction Studies of NiTi-based High Temperature Shape Memory Alloys

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High Temperature Shape Memory Alloys (HTSMAs)

- Part of SMA research at NASA GRC is directed toward the development of HTSMAs, understanding and predicting their macroscopic and microstructural behavior, and introducing them into large scale commercial devices.

**Objectives:**
- Targeted HTSMA development to meet device requirement
- To do that, we must provide links between the macroscopic behavior and the underlying micromechanics (*in situ* neutron and synchrotron X-ray Diffraction)
- Extension to low temperature and cryogenic SMAs
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$)

- Why Hf?
  - HTSMA (No precious metals)
  - Af > 150 °C (can be modified to lower temperatures)
  - Little or no training required (inherent dimensional stability)
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isothermal Response

No plastic strain up to the tested 1GPa

$E_{\text{load}} = 58$ GPa

$E_{\text{unload}} = 61$ GPa

Sample 1: 72 cycles
Sample 2: 85 cycles

Heat + cool

30 ºC
60 ºC
90 ºC
120 ºC
140 ºC
200 ºC
220 ºC
240 ºC
260 ºC

Good superelasticity
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isothermal Response

No plastic strain up to the tested 1GPa

$E_{load} = 58$ GPa
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Sample 1: 72 cycles
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Good superelasticity
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (C)

Macroscopic

![Graph showing temperature and stress over time with displacement and no-load TT's](image-url)

- $A_s = 158 ^\circ C$
- $A_f = 178 ^\circ C$
- $M_s = 148 ^\circ C$
- $M_f = 132 ^\circ C$

Macroscopic vs. Microscopic
In situ Diffraction

**NEUTRON DIFFRACTION**
Los Alamos National Laboratory (LANL)
Spectrometer for MAterials Research at Temperature and Stress (SMARTS)

**SYNCHROTRON X-RAY DIFFRACTION**
Helmholtz-Zentrum Geesthacht (PETRA III)
High Energy Materials Science Beamline (HEMS)

Sample

2D detector

Debye–Scherrer diffraction rings

Integrated diffraction pattern

Debye–Scherrer diffraction rings

Load

2D detector

Diffraction angle (2\(\theta\))

(011)

(100)

(111)

(102)

Intensity (a.u.)

0

1

\(\sigma, \varepsilon\)

neutron beam
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response (B2)

*In situ* Synchrotron Diffraction (C)

- {100}$_A$
- {110}$_A$
- {111}$_A$

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- 0 MPa, 300 °C
- 100 MPa, 300 °C
- 200 MPa, 300 °C
- 0 MPa, 300 °C
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B2) No Plastic Strain
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response (B2) \{211\}_A

- 0 MPa (Unload)
- 0 MPa
- 100 MPa
- 200 MPa

- 0 MPa, 300 °C
- 100 MPa, 300 °C
- 200 MPa, 300 °C
- 0 MPa, 300 °C
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response (B2)

- $A_s = 158 \, ^\circ\text{C}$
- $A_f = 178 \, ^\circ\text{C}$
- $M_s = 148 \, ^\circ\text{C}$
- $M_f = 132 \, ^\circ\text{C}$

No-load TT's

Displacement (mm)
Temperature (°C)

0 MPa
0 MPa-post
100 MPa
200 MPa

0 100 200 300

Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B2)
**Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B2)**

**In situ Synchrotron (C)**

- **{110}$_A$**
  - Stress (MPa) vs. lattice strain (%)
  - Planes //

- **{210}$_A$**
  - Stress (MPa) vs. lattice strain (%)
  - Planes ⊥

**In situ Neutron (T)**

- Stress (MPa) vs. lattice strain (%)
- Planes //
- Planes ⊥
- 280°C
Ni-Rich (Ni\textsubscript{50.3}Ti\textsubscript{29.7}Hf\textsubscript{20}) Isobaric Response (B19') Texture Evolution in Martensite

(normalized intensity $I/I_o$)

- (011)$_M$
- (110)$_M$
- (021)$_M$
- (030)$_M$
- (131)$_M$
Ni-Rich (Ni₅₀.₃Ti₂₉.₇Hf₂₀) Isobaric Response (B₁₉')

In situ Synchrotron (C)

In situ Neutron (T)

(a)

(b)
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Summary

Precipitates are Key

*SEM*

- Fine, nanometer size, coherent precipitate phase (through stoichiometry control and aging)
- Limited detwinning attributed to the pinning of twin and variant boundaries by the dispersion of fine precipitates
- Efficient obstacles to irreversible plastic deformation
- Precipitate phase is believed to be the stabilizing factor in this alloy
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$)- Literature

Microstructural Response During Isothermal and Isobaric Loading of a Precipitation-Strengthened Ni-29.7Ti-20Hf High-Temperature Shape Memory Alloy

O. BENAFAN, R.D. NOEBE, S.A. PADULA II, and R. VAIDYANATHAN

Fan Yang; Daniel R Coughlin; Patrick J Phillips; Limei Yang; Arun Devaraj; Libor Kovarik; Ronald D Noebe; Michael J Mills

Structure analysis of a precipitate phase in a Ni rich high temperature NiTiHf shape memory alloy, Acta Mat., accepted

Load-biased shape-memory and superelastic properties of a precipitation strengthened high-temperature Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$ alloy

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Characterization of the microstructure and mechanical properties of a 50.3Ni–29.7Ti–20Hf shape memory alloy

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Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$)

- Extruded and aged
- No major aging effects (single phase)
Ni(Pd)-Rich ($\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$)

TEM images show no precipitate phase (Ext. 159)

- Martensite phase
- Antiphase domain boundaries
- No precipitates
Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) Isobaric Response

Macroscopic

- 2 thermal cycles at 0 MPa
- 10 thermomechanical cycles at 300 MPa
- 4 thermal cycles at 0 MPa (TWSME)
Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) TWSME Texture Retained After Unloading

- **Ni(Pd)-Rich** (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) TWSME
- **Texture Retained After Unloading**

**Graphical Representation**

- **Cycle 0**: No load
- **Cycle 1**: Load cycle
- **Cycle 2**: Load cycle
- **Cycle 3**: Load cycle
- **Cycle 4**: Load cycle
- **Cycle 5**: Load cycle
- **Cycle 6**: Load cycle
- **Cycle 7**: Load cycle
- **Cycle 8**: Load cycle
- **Cycle 9**: Load cycle
- **Cycle 10**: Load cycle

**Color Scale**

- 14.0
- 12.0
- 10.0
- 8.0
- 6.0
- 4.0
- 2.0
- 0.0

**Load Conditions**

- **300 MPa**

**Legend**

- **Max**: Maximum value
- **Min**: Minimum value

**No Load Conditions**

- **No load**

**Cycle Specifics**

- **Cycle 0**: No load
- **Cycle 1**: Load cycle
- **Cycle 2**: Load cycle
- **Cycle 3**: Load cycle
- **Cycle 4**: Load cycle
- **Cycle 5**: Load cycle
- **Cycle 6**: Load cycle
- **Cycle 7**: Load cycle
- **Cycle 8**: Load cycle
- **Cycle 9**: Load cycle
- **Cycle 10**: Load cycle

**Color Gradient**

- White to Red

**Data Points**

- White to Red gradient

**Graphical Analysis**

- Comparative analysis of load and no load conditions
- Retention of texture after unloading

**Conclusion**

- Texture retention after multiple load cycles
- Comparison of load and no load conditions
Ni(Pd)-Rich (Ni\textsubscript{24.3}Ti\textsubscript{49.7}Pd\textsubscript{26}) Isobaric Response
Retained Martensite at 300 °C
Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) Summary

HTSMA with TWSME

TEM

Neutron diffraction

- No Precipitates formed after aging at 400 °C
- Large amount of dislocations present after load-bias tests
- Stabilized twins at room temperature responsible for TWSME
HTSMAs Summary

- **Ni-Rich NiTiHf: Good stability**
  - Neutron, X-ray and electron diffraction confirmed the formation of fine, nanometer size, coherent precipitates through careful stoichiometry control and aging. This precipitate phase is believed to be the stabilizing factor in this $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy.

- **Ni-Rich NiTiPd: Good TWSME**
  - Composition control on the Ni(Pd)-Rich ($\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$) resulted in a good TWSME, but unstable biased actuation.

- **Choice of alloy based on application:**
  - Targeted alloy design to meet application requirement can be done to optimize properties.

- Diffraction data served to provide a link between microscopic and macroscopic behavior, and supply information pertinent to the proper formulation of SMA micromechanics models.
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Thank you