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 ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$)

Why Hf?

- HTSMA (No precious metals)
- $A_f > 150 \, ^\circ C$ (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

$E_{load} = 58$ GPa
$E_{unload} = 61$ GPa

Sample 1: 72 cycles
Sample 2: 85 cycles

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

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

**Macroscopic**

![Graph showing temperature and stress with displacement and time axes.]

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

- 0 MPa
- 100 MPa
- 200 MPa

No-load TT's

**Microscopic**

![Graph showing temperature and stress with time axis.]

- 0 MPa
- 100 MPa
- 200 MPa

- 0 MPa-post

Intensity (a.b.)
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)
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B2)

In situ Synchrotron Diffraction (C)
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B2) No Plastic Strain

- {211}_A
- {200}_A
- {210}_A
- {111}_A
- {110}_A
- {100}_A

0 MPa, 300 ºC
0.5
0
-0.5
-1

0 MPa, 300 ºC
100 MPa, 300 ºC
200 MPa, 300 ºC

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Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response ($\text{B2}$) $
\{211\}_A$

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

lattice strain (%)
Ni-Rich (Ni\textsubscript{50.3}Ti\textsubscript{29.7}Hf\textsubscript{20}) Isobaric Response (B2)

\begin{align*}
A_s &= 158 \, ^\circ\text{C} \\
A_f &= 178 \, ^\circ\text{C} \\
M_s &= 148 \, ^\circ\text{C} \\
M_f &= 132 \, ^\circ\text{C}
\end{align*}
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response (B2)

**In situ Synchrotron (C)**

**In situ Neutron (T)**

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**Planes //**

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>Lattice Strain (%)</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
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280 °C

**Planes \(\perp\)**

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280 °C
Ni-Rich (Ni_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}) Isobaric Response (B19')
Texture Evolution in Martensite
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$) Isobaric Response (B19')

**In situ Synchrotron (C)**

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**In situ Neutron (T)**

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(a)  

(b)
Ni-Rich (Ni$_{50.3}$Ti$_{29.7}$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

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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 ($\text{Ni}_{24.3}\text{Ti}_{49.7}\text{Pd}_{26}$)

- 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

No load cycle 0

Load cycle 2

300 MPa cycle 2

Unload cycle 1

No load cycle 1

Load cycle 3

300 MPa cycle 3

Unload cycle 2

No load cycle 2

Load cycle 4

300 MPa cycle 4

Unload cycle 3

No load cycle 3

Load cycle 5

300 MPa cycle 5

Unload cycle 4

No load cycle 4

Load cycle 6

300 MPa cycle 6

Unload cycle 1

No load cycle 1

Load cycle 7

300 MPa cycle 7

Unload cycle 2

No load cycle 2

Load cycle 8

300 MPa cycle 8

Unload cycle 3

No load cycle 3

Load cycle 9

300 MPa cycle 9

Unload cycle 4

No load cycle 4
Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) Isobaric Response
Retained Martensite at 300 ºC

(a) 100 reflection
(b) 002$_M$ reflection
Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$Pd$_{26}$) Summary
HTSMA with TWSME

**TEM**

- 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

**Neutron diffraction**
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 Ni$_{50.3}$Ti$_{29.7}$Hf$_{20}$ alloy

- **Ni-Rich NiTiPd: Good TWSME**
  - Composition control on the Ni(Pd)-Rich (Ni$_{24.3}$Ti$_{49.7}$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