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)
  - \(\text{Af} > 150 \, ^\circ\text{C}\) (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 1 GPa

Heat + cool

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

Sample 1: 72 cycles
Sample 2: 85 cycles

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

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

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Good superelasticity

Sample 1: 72 cycles
Sample 2: 85 cycles
Ni-Rich (Ni\textsubscript{50.3}Ti\textsubscript{29.7}Hf\textsubscript{20}) Isobaric Response (C)

Macroscopic

![Macroscopic Response Graph]

Temperature (°C) vs. Stress (MPa) graph showing:
- \(A_s = 158 \, ^\circ C\)
- \(A_f = 178 \, ^\circ C\)
- \(M_s = 148 \, ^\circ C\)
- \(M_f = 132 \, ^\circ C\)

Displacement (mm) vs. Temperature (°C) graph showing:
- No-load TT's
- 0 MPa
- 100 MPa
- 200 MPa
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)

neutron beam

\[ \sigma, \varepsilon \]

Integrated diffraction pattern

Debye–Scherrer diffraction rings

2D detector
Ni-Rich ($\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$) Isobaric Response (B2)

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

{211}_A

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

![Graph showing isobaric response of Ni-Rich alloy](image)

- Displacement (mm) vs. Temperature (ºC)
- No-load TT's
- $A_s = 158$ ºC
- $A_f = 178$ ºC
- $M_s = 148$ ºC
- $M_f = 132$ ºC

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

**In situ Synchrotron (C)**

![Graph showing lattice strain vs. stress for planes // and \perp to lattice planes at 280 °C](image)

**In situ Neutron (T)**

![Graph showing lattice strain vs. stress for planes // and \perp to lattice planes at 280 °C](image)
Ni-Rich (Ni_{50.3}Ti_{29.7}Hf_{20}) Isobaric Response (B19') Texture Evolution in Martensite

- (011)_M
- (110)_M
- (021)_M
- (030)_M
- (131)_M

Normalized intensity (I/I_o)

- 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 (B19')

**In situ Synchrotron (C)**

- $(011)_M$
- $(131)_M$

**In situ Neutron (T)**

- 0 MPa initial
- 400 MPa no thermal cycle
- 400 MPa thermal cycle 1
- 400 MPa thermal cycle 2
- 400 MPa thermal cycle 3
- 0 MPa after no load thermal cycle

Ni-rich composition and isobaric response data.
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

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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 (Ni$_{24.3}$Ti$_{49.7}$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$_{26}$) Isobaric Response
Retained Martensite at 300 ºC

(a) Normalized intensity (arbitrary units)

(b) Normalized intensity (arbitrary units)
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
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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