ASSESSMENT OF SHAPE MEMORY ALLOYS – FROM ATOMS TO ACTUATORS – VIA IN SITU NEUTRON DIFFRACTION

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It Takes a Team…

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Motivation and Objectives

• We examine microstructures of:
  • Conventional structural materials by quenching in the high temperature structure and examining at room temperature.
  • This cannot be done for SMA’s because of the diffusionless phase transformation (austenite/martensite) cannot be suppressed by quenching

• Neutrons are non-destructive: complete, intact specimens/components can be studied in small samples (~mm) or in bigger engineering components (~m)

WE MUST EXAMINE IN SITU AT STRESS AND TEMPERATURE
Length Scale in Engineering Materials
Where Does Neutron Diffraction Fit?

ATOMIC SCALE
(NANOMATERIALS)

10^{-10} Å

10^{-9} nm

10^{-8}

10^{-7} μm

10^{-6} mm

10^{-5}

10^{-4}

10^{-3}

10^{-2}

10^{-1}

10^0 m

MICRO-SCALE
(MICROSTRUCTURES)

TEM

SEM / FIB

OM

HRTEM / STEM

ATOM PROBE / FIM

STRUCTURAL SCALE
(COMPLEX COMPONENTS)

LOAD FRAMES

NEUTRON / X-RAY DIFFRACTION

0%

5%

10%

15%

20%

stress (MPa)

strain (%)
Applications of Neutron Diffraction

- Chemistry
- Physics
- Engineering
- Life sciences
- Biosciences
- Materials science
- Geological sciences
- Archeology

Courtesy: Mario Bieringer
Neutrons at the Experimental Area

• Now we have neutrons, what next?

| Neutron beam: $E_0, \vec{k}_0$ | Detector: $E, \vec{k}$ |

- Neutron beam with a known wavevector ($k_0$) and energy ($E_0$)
- Detect number of scattered neutrons with a wavevector ($k$) as a function of the scattering function $S(Q, \omega)$

$|Q| = \left| \vec{k}_0 - \vec{k} \right| = \frac{4\pi \sin \theta}{\lambda}$

$\Delta E = E_0 - E = \hbar \omega = \hbar^2 \left( \frac{k_0^2 - k^2}{2m} \right)$

Nomenclature

- $k$: wavevector
- $E$: energy
- $Q$: scattering vector
- $\hbar$: reduced Planck constant
- $m$: mass ($1.67 \times 10^{-24}$g)
- $\lambda$: wavelength
- $2\theta$: scattering angle

$n\lambda = 2d \sin \theta$
Neutron Diffraction Data

- **Peak position**
  - Elastic lattice strain
  - Intergranular strains

- **Peak intensity**
  - Texture changes
  - Phase fraction

- **Peak width**
  - Qualitative information

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  - Qualitative information
Neutron/Synchrotron Sources in the USA
Neutron and Synchrotron Sources Around the World
Oak Ridge National Laboratories-SNS

Spallation Neutron Source at Oak Ridge National Laboratory

The world’s most intense pulsed, accelerator-based neutron source

**Backscattering Spectrometer (BASIS) - BL-2**
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
Eugene Marenco - 865.241.1089 - marenco@ornl.gov

**Nanoscale-Ordered Materials Diffractometer (NOMAD) - BL-1B**
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Jaeck Neuhofer - 865.241.1465 - neuhoferj@ornl.gov

**Wide Angular-Range Chopper Spectrometer (WARRCS) - BL-18**
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Doug Almenrath - 865.576.9105 - almenrathd@ornl.gov

**Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) - BL-17**
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Garret Grasonoth - 865.576.0900 - grasonothg@ornl.gov

Life sciences, polymers, materials science, earth and environmental sciences
Michael Ayers - 865.576.0905 - mayerms@ornl.gov

**Vibrational Spectrometer (VISION) - BL-16B (2012)**
Vibrational dynamics in molecular systems, chemistry
Christian Wettig-Draht - 865.576.8476 - wettigdrahtc@ornl.gov

**Neutron Spin Echo Spectrometer (NSE) - BL-15**
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Michael Gant - 865.576.8460 - gantm@ornl.gov

**Hybrid Polarized Beam Spectrometer (HYPENS) - BL-14B**
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Gary Wies - 865.241.6018 - wiesga@ornl.gov

**Magnetism Reflectometer (MAGICS) - BL-4A**
Chemistry, magnetism of layered systems and interfaces
Valera Leazer - 865.576.5390 - leazerv@ornl.gov

**Liquids Reflectometer - BL-4B**
Interfaces in complex fluids, polymers, chemistry
John Ainger - 865.576.6102 - aingerj@ornl.gov

**Cold Neutron Chopper Spectrometer (CNCS) - BL-5**
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Georg Chenes - 865.576.3311 - chenesg@ornl.gov

**Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) - BL-6**
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William Heber - 865.241.0695 - heberw@ornl.gov

**Elastic Diffuse Scattering Spectrometer (CORELLI) - BL-9 (2014)**
Detailed studies of disorder in crystalline materials
Tae-Soo - 865.576.5901 - yifei@ornl.gov

**Macromolecular Neutron Diffractometer (MANDI) - BL-11 (2013)**
Atomic-level structures of membrane proteins, drug complexes, DNA
Logan Coates - 865.933.0180 - coatesl@ornl.gov

**Powder Diffractometer (PDQGEN) - BL-11A**
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Kash Hug - 865.241.7521 - hugka@ornl.gov

**Engineering Materials Diffractometer (VULCAN) - BL-7**
Mechanical behaviors, materials science, materials processing
Ko An - 865.815.3236 - keen@ornl.gov

**Spallation Neutrons and Pressure Diffractometer (SNAP) - BL-3**
Materials science, geology, earth and environmental sciences
Chris Tuls - 865.576.7168 - tulscc@ornl.gov

**LEGEND**
- **Installed, commissioning, or operating**
- **In design or construction**
- **Under consideration**
Isothermal Deformation - Loading Actuators

Binary 55NiTi

Graph showing stress (MPa) vs. strain (%) with two curves:
- Red curve: martensite (30 °C)
- Blue curve: austenite (320 °C)
Isothermal Deformation - Loading Actuators

The diagram shows the behavior of material planes under load and unload conditions. The graphs represent strain (%), load, and d-spacing (Å) with intensity (a.u.) on the y-axis. The material planes are marked with (011)_M, (100)_M, (110)_M, (020)_M, (111)_M, (111)_M, (120)_M, (121)_M, (120)_M, (030)_M, (031)_M, (013)_M, (230)_M, and (150)_M. The different colors indicate varying intensity levels, with red and blue colors being prominent. The graph also highlights the phase transitions between martensite (30 °C) and austenite (320 °C) phases.
Deformation mechanisms revealed - complexity and multiplicity of mechanisms can’t be resolved another way
- e.g., reorientation planes/limits, stress-induced-martensite region, martensite desist...
Isothermal Deformation – Where to Load Actuators? Does it Matter?

- No major differences in transformation strains
- Large strain evolution (ratcheting) difference

SMA Properties – Can they be Optimized for Actuators?

1. Material and Geometry
   - Binary 55NiTi $\rightarrow \phi = 5.08\text{mm (0.2in)}$
   - Stress free transformation temperatures
     - $A_s = 92 \, ^\circ\text{C}$
     - $A_f = 105 \, ^\circ\text{C}$
     - $M_s = 71 \, ^\circ\text{C}$
     - $M_f = 55 \, ^\circ\text{C}$
   - Effective coefficient of thermal expansion
     - $\alpha_A^* = 13.0 \times 10^{-6} / ^\circ\text{C}$
     - $\alpha_M^* = 6.4 \times 10^{-6} / ^\circ\text{C}$
   - Effective elastic moduli
     - $E_A^* = 74 \, \text{GPa}$
     - $E_M^* = 50 \, \text{GPa}$
   - Effective Poisson’s ratios
     - $\nu_A^* = 0.33$
     - $\nu_M^* = 0.387$
• Transformation temperatures during the reverse transformation measured from strain-temperature and DSC data were found to differ from the actual onset of transformation as revealed from neutron spectra.

• The austenite phase starting to form at ~75 °C,

O. Benafan et al., *Scripta Materialia*, 2013 68(18), p. 571–574
Dynamic Young’s Modulus for Ni\textsubscript{49.9}Ti\textsubscript{50.1}

- Dynamic Young’s modulus data obtained from the impulse excitation of vibration tests.
- The average dynamic modulus of martensite at room temperature was about 70 GPa, but decreased with increasing temperature with an average minimum value of 60 GPa at ~80 ºC.

O. Benafan et al., *Scripta Materialia*, 2013 68(18), p. 571–574
0.2% Offset “Yield” Stress Behavior of Ni\textsubscript{49.9}Ti\textsubscript{50.1}

- The onset of inelastic deformation (generally referred to as ‘yield’) in the martensite phase is dominated by reorientation and detwinning mechanisms.
- Decrease with increasing temperature, reaching an averaged minimum value of 140 MPa between 65 and 80 °C.
- The onset stress then sharply increased in the two-phase region and reached near saturation (with a still slightly positive slope) at 350 MPa near 130 °C.
- Inelastic deformation over this temperature range (~90 – 130 °C), which includes the B19'→B2 phase transition, is attributed to the nearly concurrent operation of stress-induced martensite and plastic deformation.
Transformation Temperatures: DSC vs. Strain-Temperature vs. Neutrons

- Transformation temperatures during the reverse transformation measured from strain-temperature and DSC data were found to differ from the actual onset of transformation as revealed from neutron spectra.
- The austenite phase starting to form at ~75 °C,

Thermomechanical Cycling of Actuators

**Electron diffraction**

**In situ diffraction**

**Outcome**

Outcome:
- In situ diffraction
- Electron diffraction

**55NiTi**

0.0 3.0 5.0 7.0 0.0 1.5 3.0

Temperature (°C)

20 cycles 50 cycles 0 cycles
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Coefficient of Thermal Expansion: Large Anisotropy

- Atomic scale measurements of thermal strains

Outcome
- First report on NiTi CTE tensor (monoclinic martensite) including negative expansion in certain crystal orientations
- Parametric input for most SMA models

**Table:**

<table>
<thead>
<tr>
<th></th>
<th>Heating ($10^{-6}/°C$)</th>
<th>Cooling ($10^{-6}/°C$)</th>
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<tbody>
<tr>
<td>$B19'$ NiTi</td>
<td></td>
<td></td>
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<tr>
<td>Thermal</td>
<td>$\alpha_{11}$</td>
<td>$\alpha_{11}$</td>
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<td>-30.8</td>
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<td>22.7</td>
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<td>$\alpha_{31}$</td>
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<td>32.4</td>
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<tr>
<td>CTE*</td>
<td>6.4</td>
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<tr>
<td>CTE†</td>
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</tr>
<tr>
<td>CTE (extensometry)</td>
<td>10.3</td>
<td>9.0</td>
</tr>
<tr>
<td>$B2$ NiTi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTE*</td>
<td>13.0</td>
<td>13.1</td>
</tr>
<tr>
<td>CTE (extensometry)</td>
<td>12.4</td>
<td>12.3</td>
</tr>
</tbody>
</table>

*isotropic average †self-consistent model

Coefficient of Thermal Expansion: Large Anisotropy

- Similar observation in HTSMAs (e.g., NiTiPt – B19)

O. Benafan et al., unpublished work
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Elastic Moduli: Hard and Soft Orientations

- Strain anisotropy and texture measurements

- Outcome
  - First validation of *ab initio* calculation
  - Entire compliance matrix, not just a Young's modulus
  - Revealed mechanisms responsible for deflated modulus values obtained from conventional macroscopic tests

Elastic Moduli: Hard and Soft Orientations

NiTiPt

O. Benafan et al., unpublished work
Elastic Moduli: Hard and Soft Orientations

NiTiPt

\[ \begin{align*}
E_{011} &= 257.8 \text{ GPa} & R &= 0.985 \\
E_{002} &= 138.7 \text{ GPa} & R &= 0.994 \\
E_{111} &= 99.2 \text{ GPa} & R &= 0.997 \\
E_{120} &= 55.1 \text{ GPa} & R &= 0.988 \\
E_{102} &= 138.3 \text{ GPa} & R &= 0.993 \\
E_{121} &= 75.3 \text{ GPa} & R &= 0.995 \\
E_{030} &= 173.0 \text{ GPa} & R &= 0.998 \\
E_{013} &= 132.3 \text{ GPa} & R &= 0.988 \\
E_{122} &= 88.3 \text{ GPa} & R &= 0.996 \\
E_{032} &= 218.6 \text{ GPa} & R &= 0.886 \\
\end{align*} \]
Optimization of Two-Way Shape Memory Effect

- Uniaxial deformation at room temperature followed by free recovery

Outcome

- Established a quick and efficient method for creating a strong and stable TWSME
- Texture maps were used to determine deformation modes – correlated with TWSME stability and magnitude (not possible another way)
Shape Setting of SMA Actuators

- In situ neutron diffraction during shape setting of bulk polycrystalline NiTi

- Outcome
  - Guidelines for shape setting any actuator: stress and temperature limits for shape setting
  - Neutrons revealed mechanisms responsible for the stress generation and relaxation during shape setting.

Torsional Characteristics of 55NiTi
Torsional Characteristics of 55NiTi

(a) angle of twist vs. temperature for $T = 5.17$ N-m

(b) angle of twist vs. temperature for $T = 0$ N-m (TWSME)

(c) angle of twist vs. temperature for $T = 5.17$ N-m

(d) angle of twist vs. temperature for $T = 0$ N-m (TWSME)

(e) Solid and tube structures with d-spacing and normalized intensity data.
Extension of Neutrons to Novel High Temperature SMAs

- Microstructural evolution during isothermal and isobaric deformation of NiTiHf

- **Outcome**
  - High work output and dimensional stability
  - Texture measurements were correlated to the lack of evolution in this alloy
  - Confirmed relationship of microstructure and load-biased tests: From Neutron spectra
  - Neutrons showed why training of Hf alloy is not necessary

The role of retained martensite during thermal-mechanical cycling in NiTiPd high temperature shape memory alloy was revealed.

- **Outcome**
  - Direct correlations were made between macroscopic changes in actuator performance parameters, and atomic-scale evolution from neutron spectra.
  - The rate of evolution of texture and volume fraction of the retained martensite plays a key role in the stability of the actuator.
Neutrons can be used to study most actuator forms.
Thank You