Project 17: Characterization of Microstructure Evolution in Nickel-Titanium-Hafnium Intermetallics

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Student: Sean Mills (Mines)

Faculty: Aaron Stebner (Mines)

Industrial Mentor(s): Christopher Dellacorte (NASA), Ronald Noebe (NASA)

Other Participants : Behnam Aminahmadi (Mines), Yu Hong (Mines), Mohsen Asle Zaeem (Mines)

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- Student: Sean Mills (Mines)
- Advisor(s): Aaron Stebner (Mines)

Project Duration

PhD: August 2015 to December 2019

- Problem: Ni-Ti alloys experience high residual stress due to rapid quenching processes. The result is cracking and machining distortion. Not quenching leads to low hardness.
- Objective: Elucidate the effect of Hf ternary alloying on metallurgy and bearing element performances.
- Benefit: Hf-alloying could lead to reduction in residual stress by eliminating the need for rapid cooling while retaining high strength and hardness levels of quenched binary Ni-Ti.

Recent Progress

- Rolling contact fatigue (RCF) tests on $Ni_{50.3}Ti_{46.7}Hf_3$ and $Ni_{56}Ti_{36}Hf_8$ and $Ni_{55}Ti_{45}$ alloy specimens
- TEM characterization of microstructure evolution in deformed $Ni_{56}Ti_{36}Hf_8$ and $Ni_{55}Ti_{45}$ alloys
- Identification and structure analysis of newly discovered Ni_3Ti_2 phase
- Uniaxial compression testing of 56 at.% Ni alloys

Metrics

Description	% Complete	Status
1. Residual stress and hardness testing on $Ni_{55}Ti_{45}$ & $Ni_{54}Ti_{45}Hf_1$ (NASA)	100%	●
2. Literature review	90%	●
3. Rolling contact fatigue characterization of $Ni_{54}Ti_{45}Hf_1$ alloy	90%	●
4. Time/Temperature/Transformation of $Ni_{54}Ti_{45}Hf_1$ alloy	50%	●
5. Alloy optimization – vary nickel and hafnium contents by 1-8 at%	85%	●

Industrial relevance

Nitinol shape-memory alloy with added hafnium resists both wear and corrosion

January 09, 2016

Source: ASM International

Puris LLC, Bruceton Mills, W. Va., recently signed a limited (partially) exclusive, term license agreement with NASA Glenn Research Center to produce a high-performance, hafnium-enhanced shape-memory powder metallurgy alloy that provides resistance to both wear and corrosion.

Marketed under the brand name SM-103, the 60NiTi(Hf) alloy demonstrates a lower residual stress than other 60 nitinol alloys, resulting in improved response to heat treatment and easier processing. It delivers resistance to both wear and corrosion, traditionally considered to be mutually exclusive, in addition to favorable load-bearing properties. These attributes make it well suited to industrial bearings and precision bearing applications.

<www.asminternational.org/web/smst/news/industry/results/-/journal_content/56/10180/26098479/NEWS>

C. DellaCorte, M. K. Stanford, R. A. Manco, and F. Thomas, “Design Considerations for Resilient Rolling Element Bearings Made From Low Modulus Superelastic Materials,” in *ASME/STLE 2011 International Joint Tribology Conference*, 2011, pp. 223–224.

Application: Water recycling system on International Space Station

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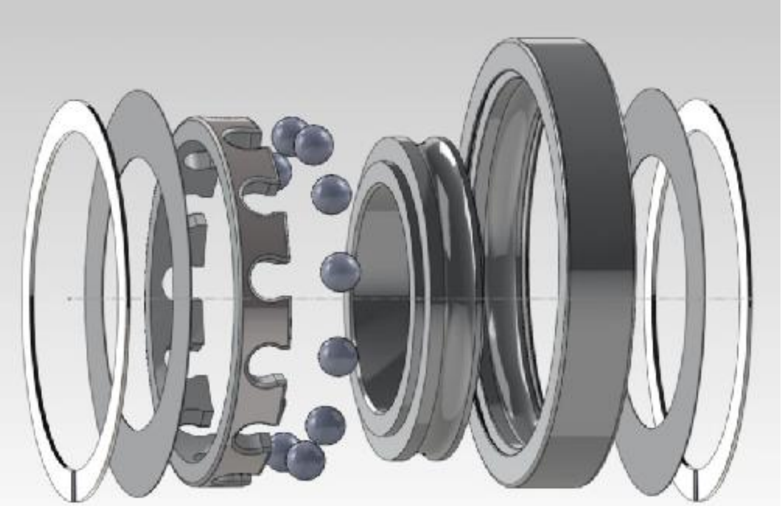
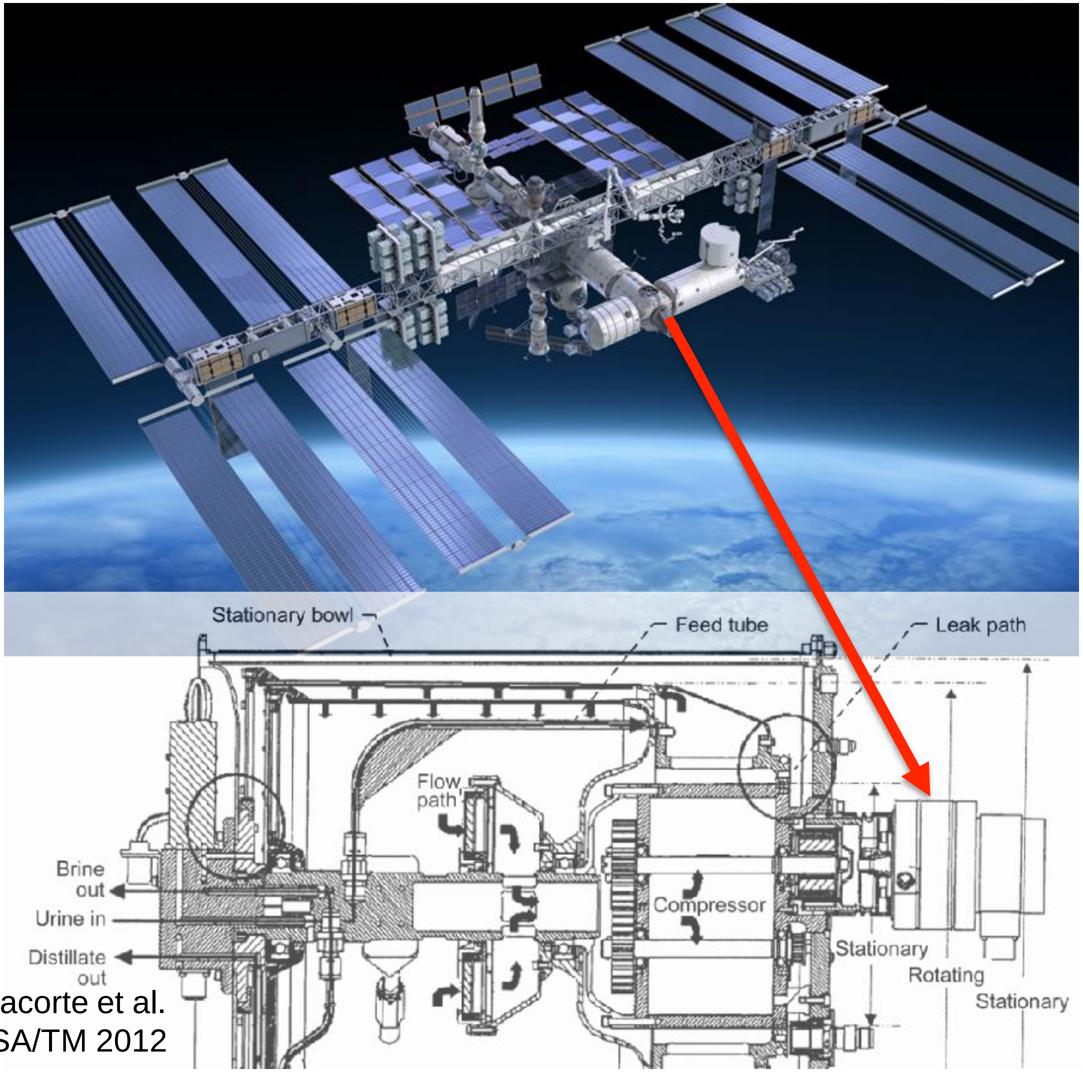
Rotating Centrifuge Bearing



Dellacorte et al.
NASA/TM 2012

Components are exposed to corrosive urine environment. Corrosion-resistant alloy system is needed!

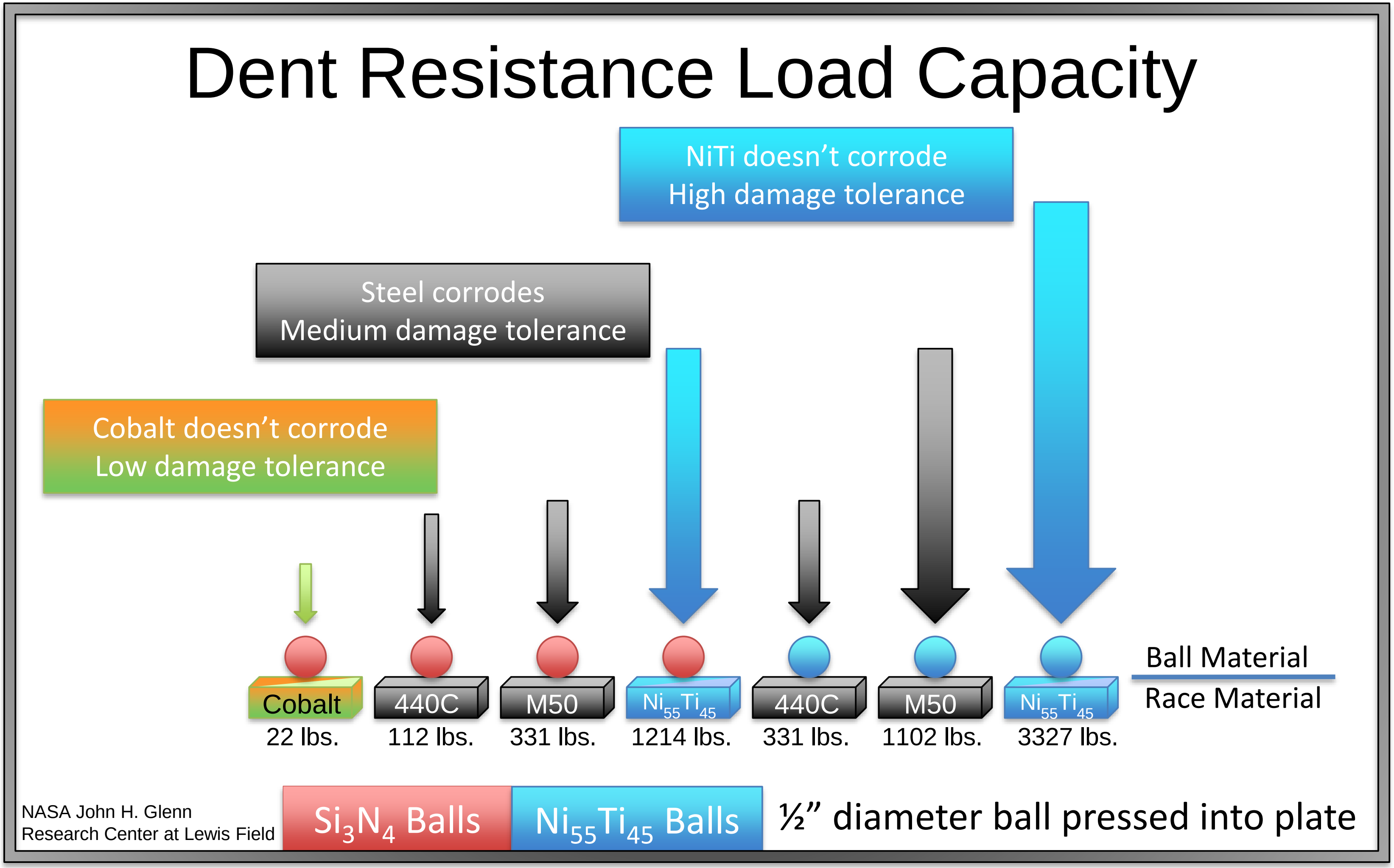


Dellacorte et al.
NASA/TM 2012

Co-Cr alloy bearings are damaged during rocket take-off

giphy.com

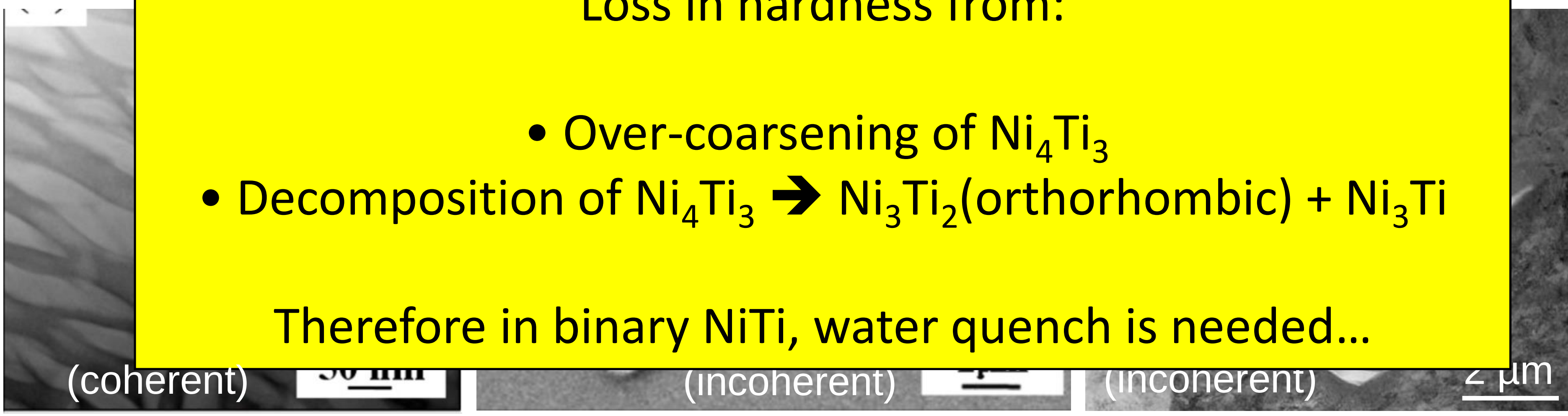
Nickel-rich Ni-Ti alloy show superior damage resistance



In 52-56 at.% NiTi alloys, stoichiometry ~Ni_4Ti_3 ➔ Rapid formation of Ni_4Ti_3

$B2_0$ ➔ $B2_1 + Ni_4Ti_3$ ➔ $B2_2 + Ni_3Ti_2$ ➔ $B2_3 + Ni_3Ti$

Precipitation process for Ni-rich NiTi (Nishida et. al 1986)



Loss in hardness from:

- Over-coarsening of Ni_4Ti_3
- Decomposition of Ni_4Ti_3 ➔ Ni_3Ti_2(orthorhombic) + Ni_3Ti

Therefore in binary NiTi, water quench is needed…

Hornbuckle et al. 2015

Benafan et al. 2017

➔ Additional aging promotes the formation of unwanted phases (Ni_3Ti_2 and Ni_3Ti)

Binary Ni-Ti bearing races are susceptible to untimely failures

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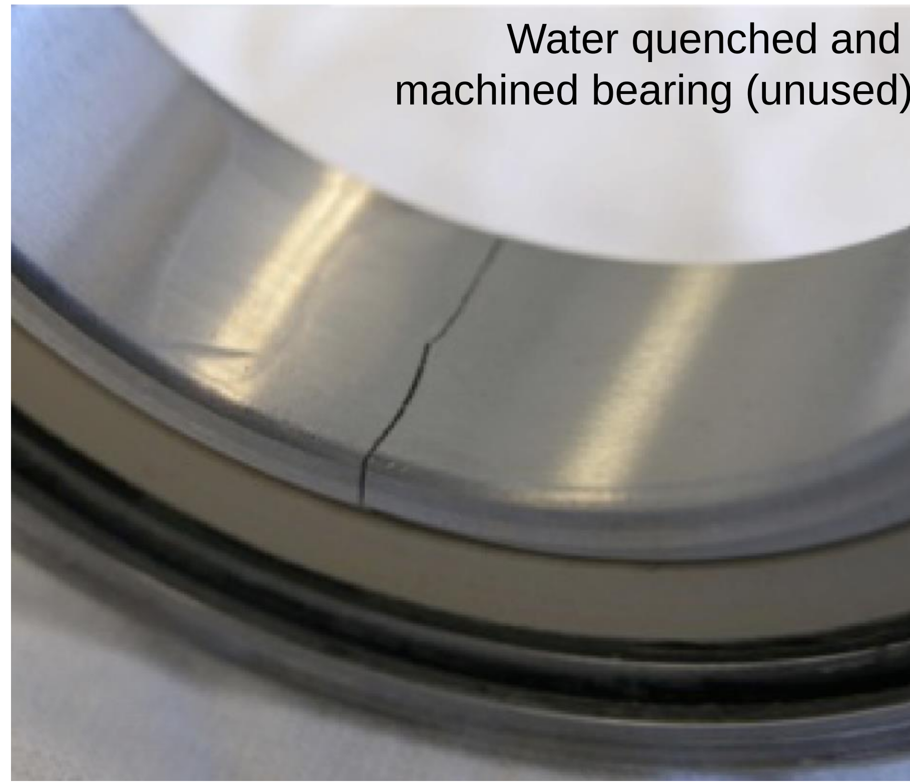

National Aeronautics a
John H. Glenn Resea

Residual stresses due to large undercooling (water quench)
➔ fracture post-machining

Subtle Hf additions in Ni-Ti

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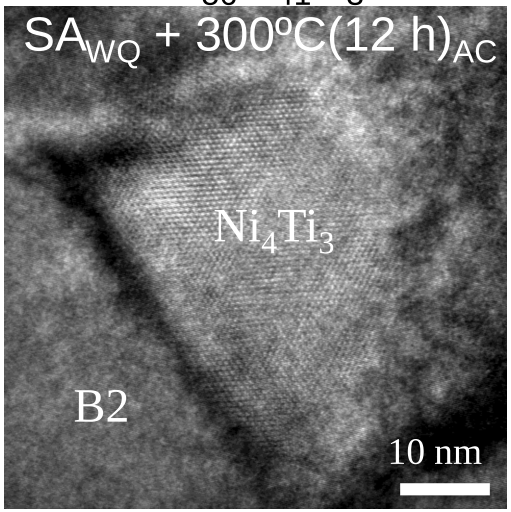
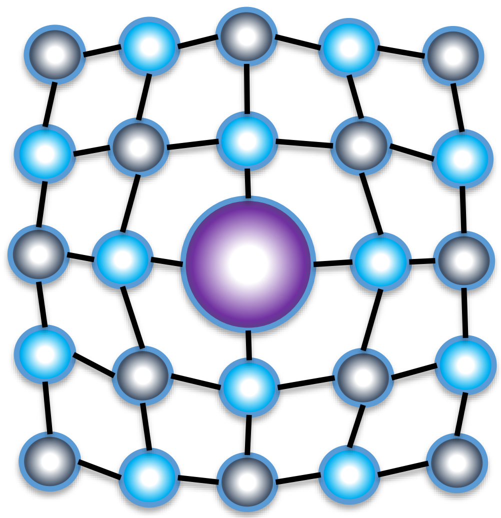
$Ni_{56}Ti_{41}H_3$

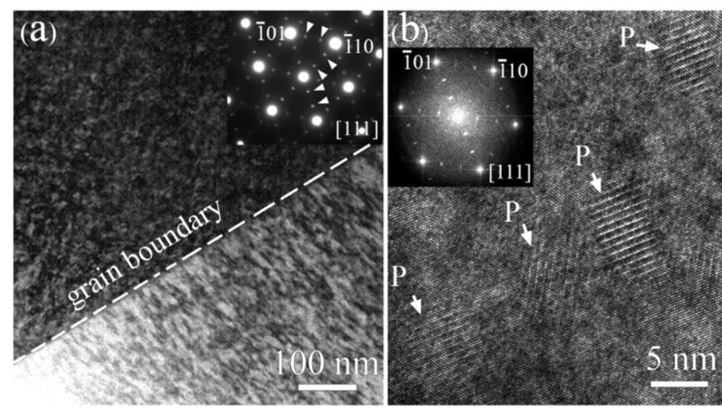


← Slows Ni_4Ti_3 kinetics (NiTiHf retains high hardness with air cooling)



← Hf solid-solution strengthening

H-phase precipitation strengthening →



B. Amin-Ahmadi et al. Scripta Mat. (2017)

Bearing grade hardness (58 – 62 HRC) is retained

Target design space of Ni-Ti-Hf

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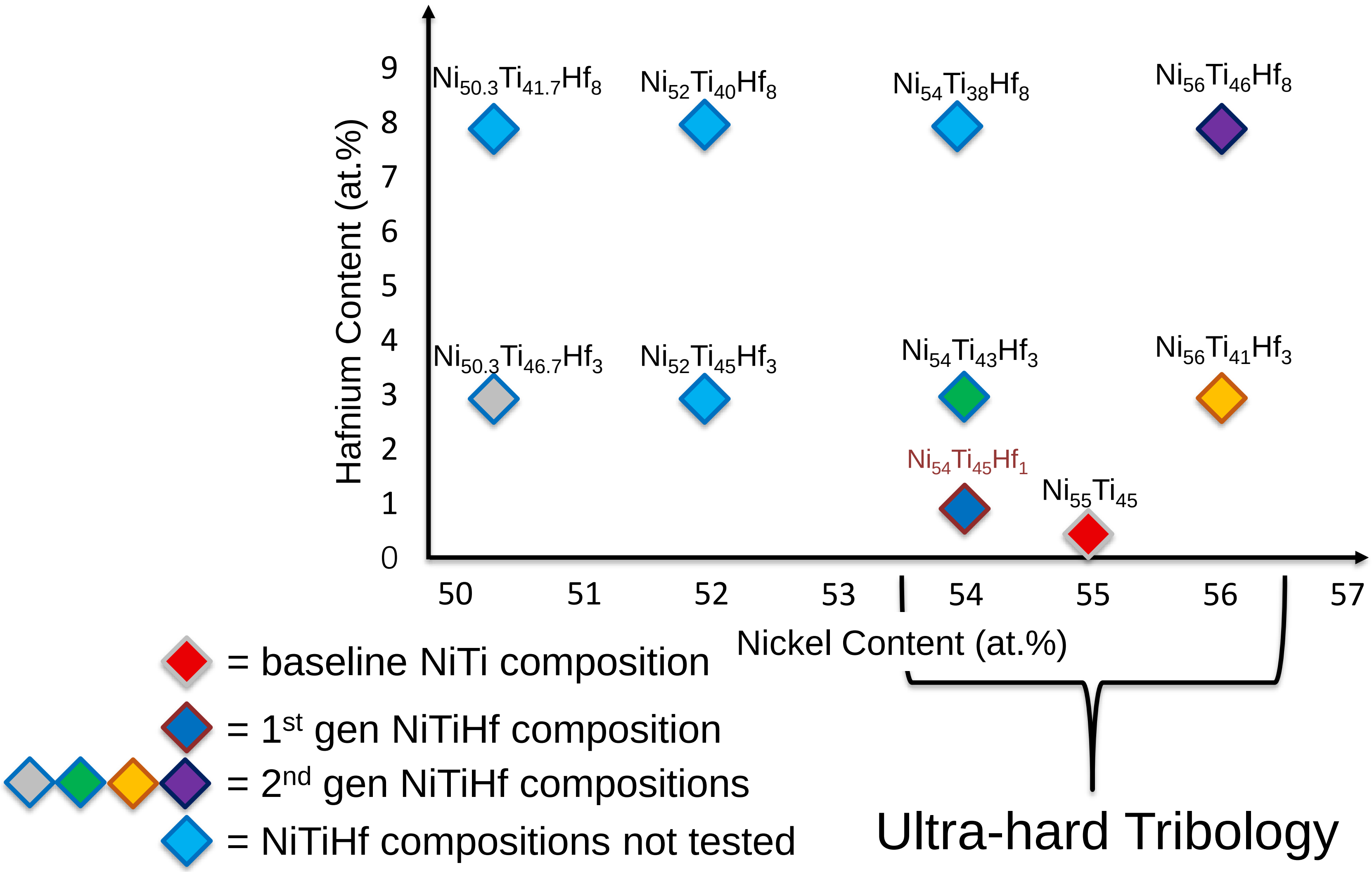
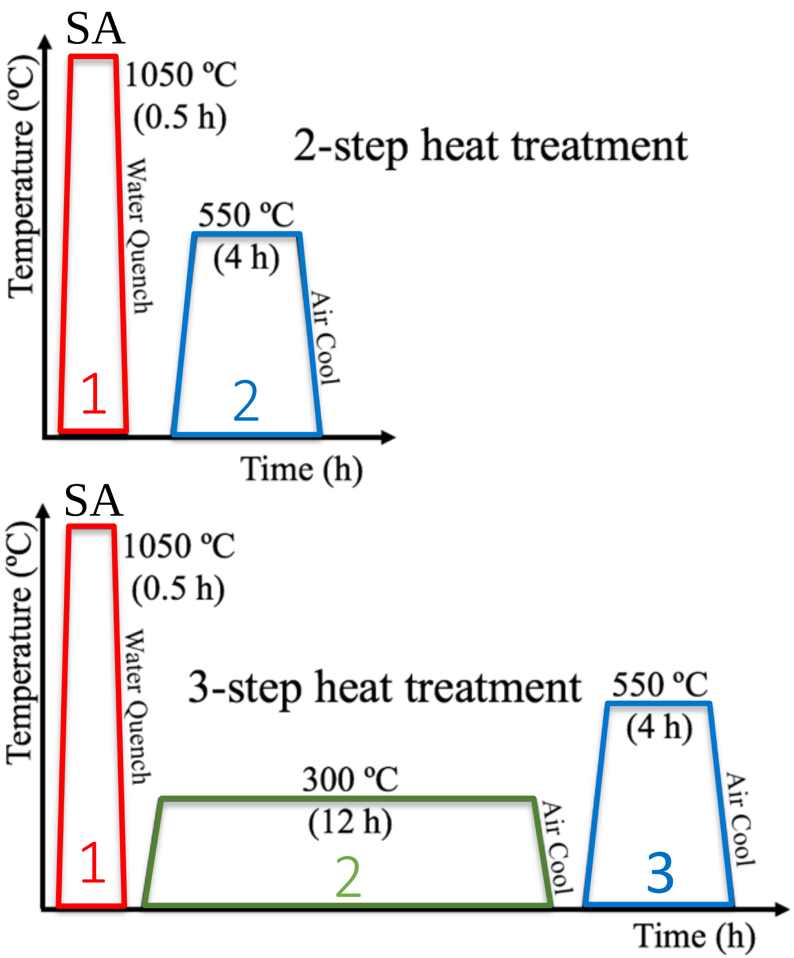
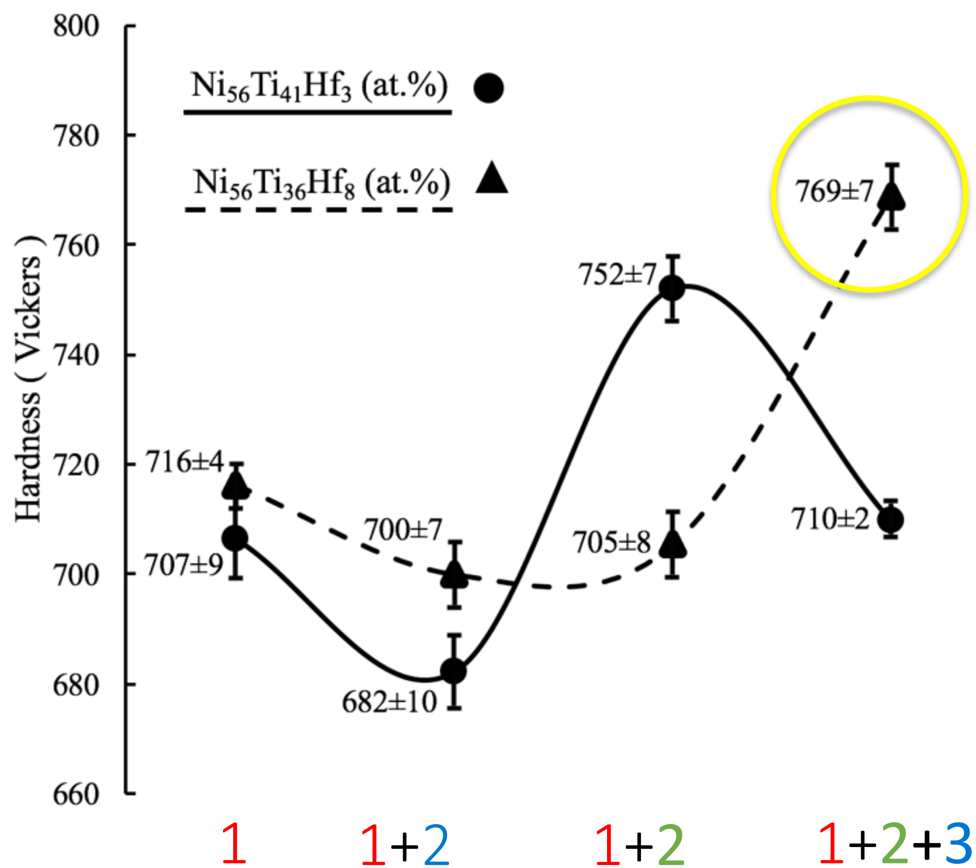


Hardness evolution not consistent between compositions

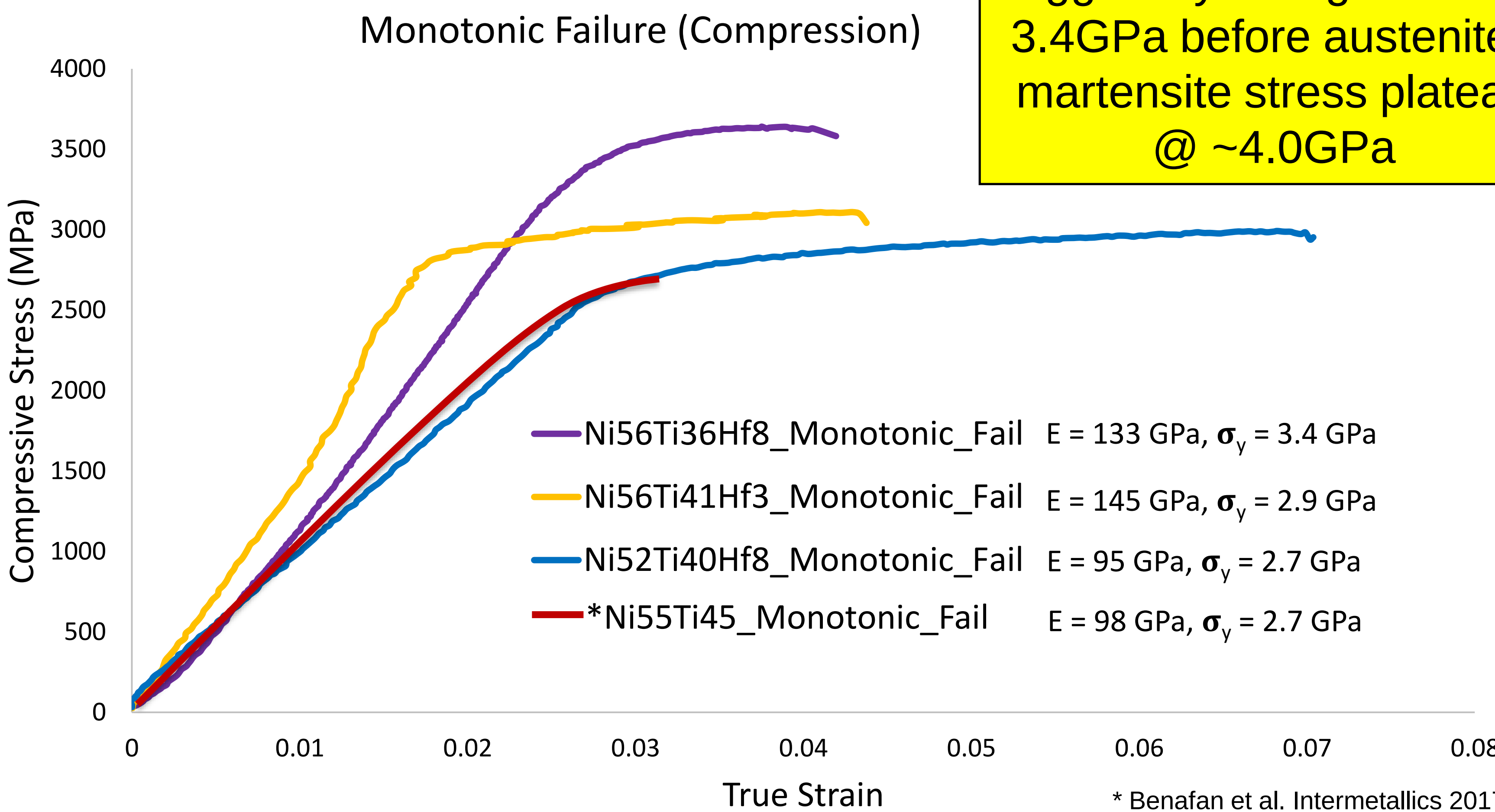




➔ $Ni_{56}Ti_{36}Hf_8$ 3-step heat treatment sample selected for further study

56 at.% Ni alloys exhibit higher moduli and transformation stresses

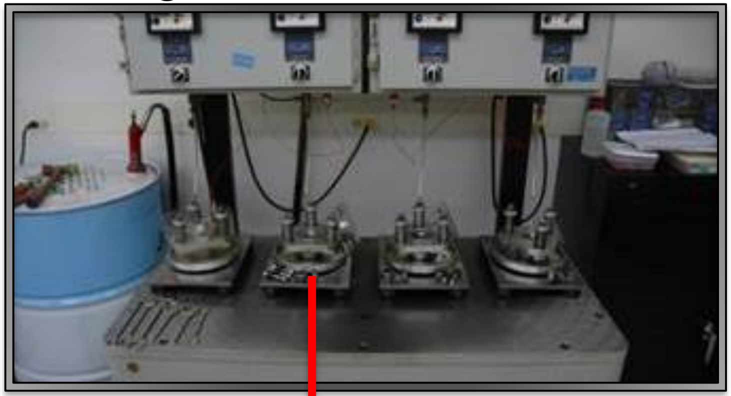
Suggests yielding occurs @ 3.4GPa before austenite–martensite stress plateau @ ~4.0GPa



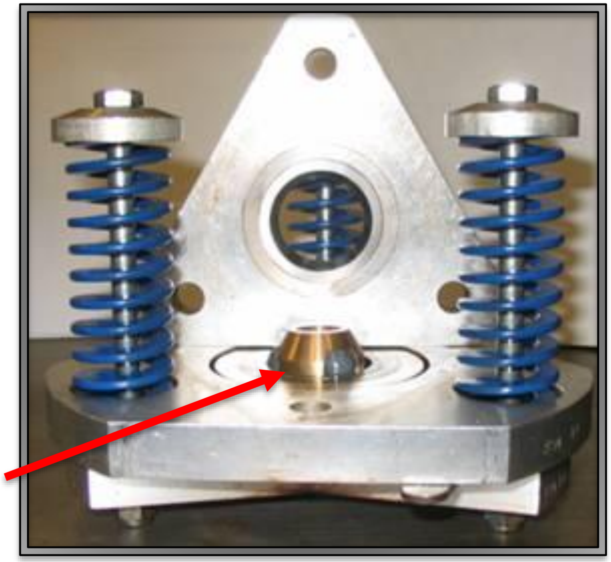
* Benafan et al. Intermetallics 2017

Rolling contact fatigue testing of Ni-Ti-Hf rods

Test rig

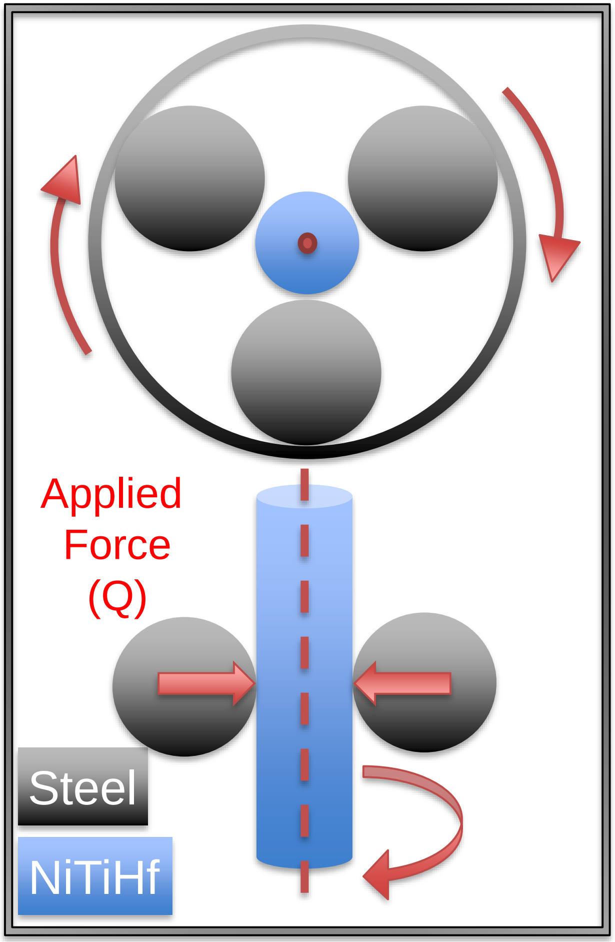


Spring loaded test head

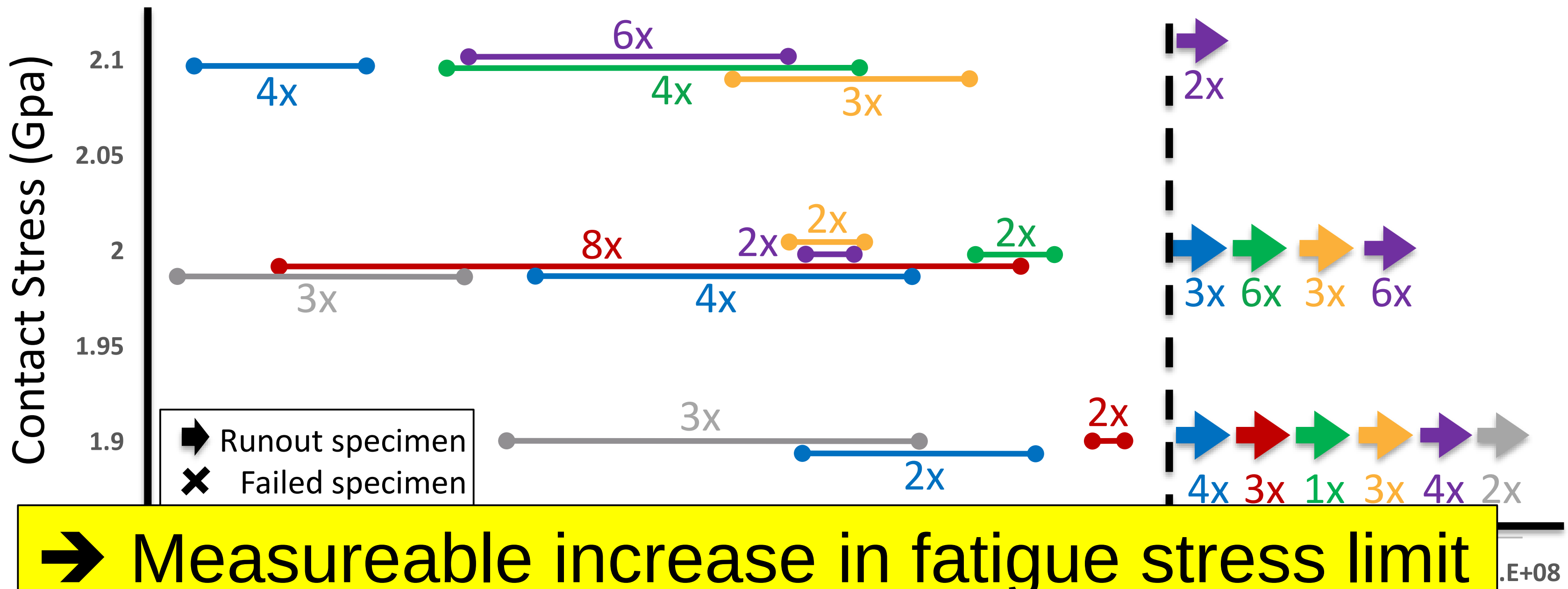


Ball bearing retainer

Three ball-on-rod RCF test configuration



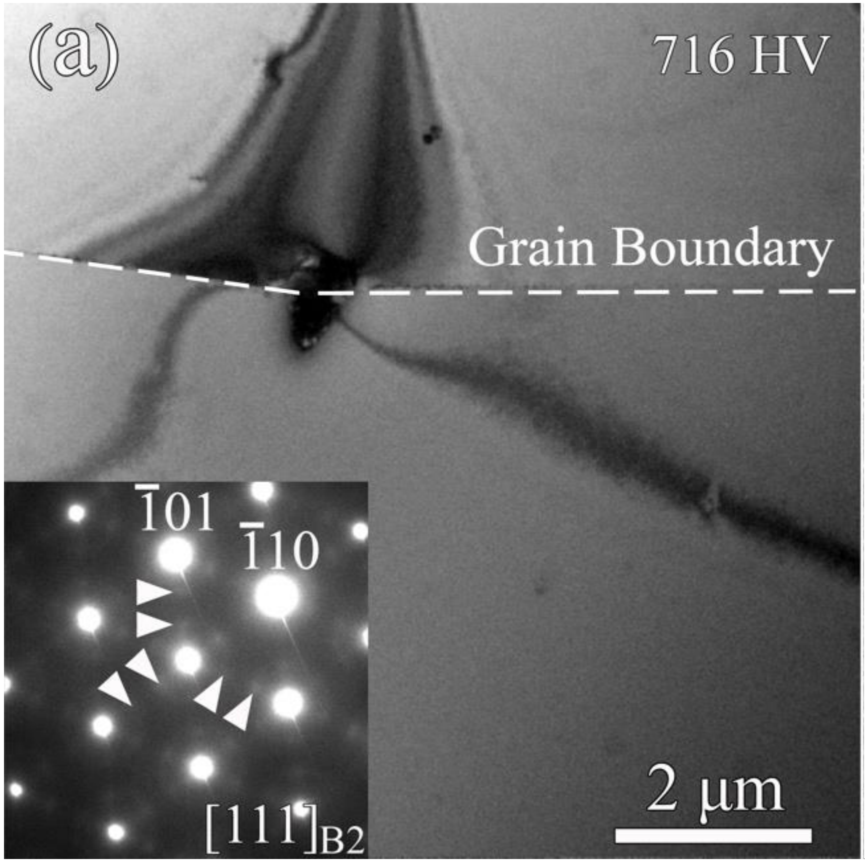
RCF Tests: Composition, surface purity and hardness



➔ Measureable increase in fatigue stress limit for $Ni_{56}Ti_{36}Hf_8$

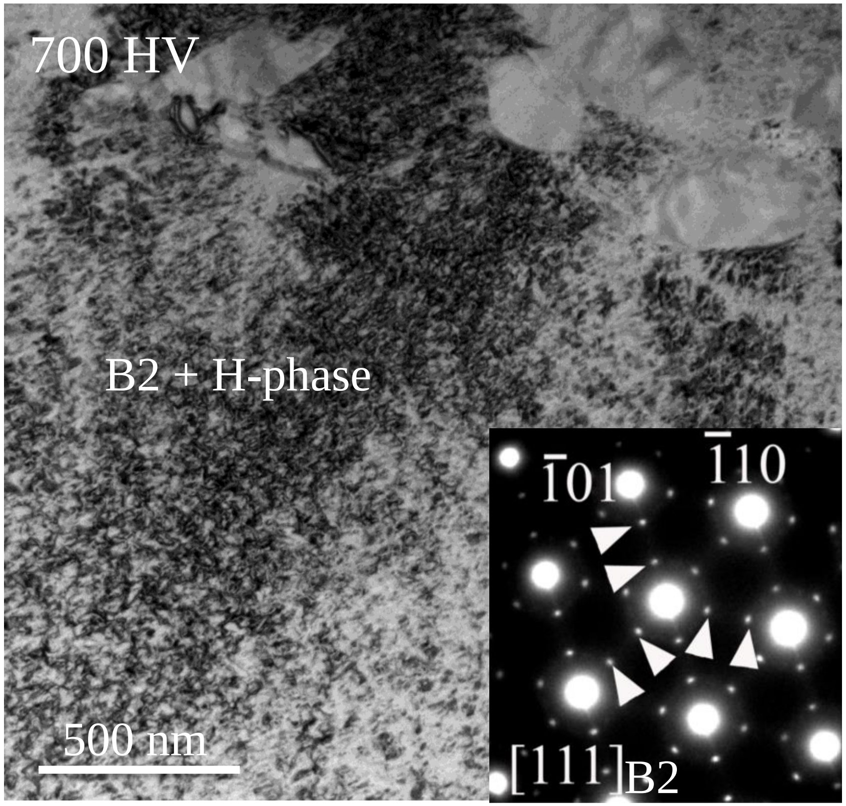
$Ni_{55}Ti_{45}$ $1000C_{WQ}$ $+400C(2h)_{AC}$ 703 HV	$Ni_{54}Ti_{45}Hf_1$ $1000C_{AC}$ $+400C(2h)_{AC}$ 677 HV	$Ni_{54}Ti_{43}Hf_3$ $1050C_{WQ}+$ $300C(12h)_{AC}$ 724 HV	$Ni_{56}Ti_{41}Hf_3$ $1050C_{WQ}+$ $300C(12h)_{AC}$ 752 HV	$Ni_{56}Ti_{36}Hf_8$ $1050C_{WQ}+$ $300C(12h)_{AC}$ $+550(4h)_{AC}$ 768 HV	$Ni_{50.3}Ti_{46.7}Hf_3$ $1050C_{WQ}+$ $300C(12h)_{AC}$ 640 HV

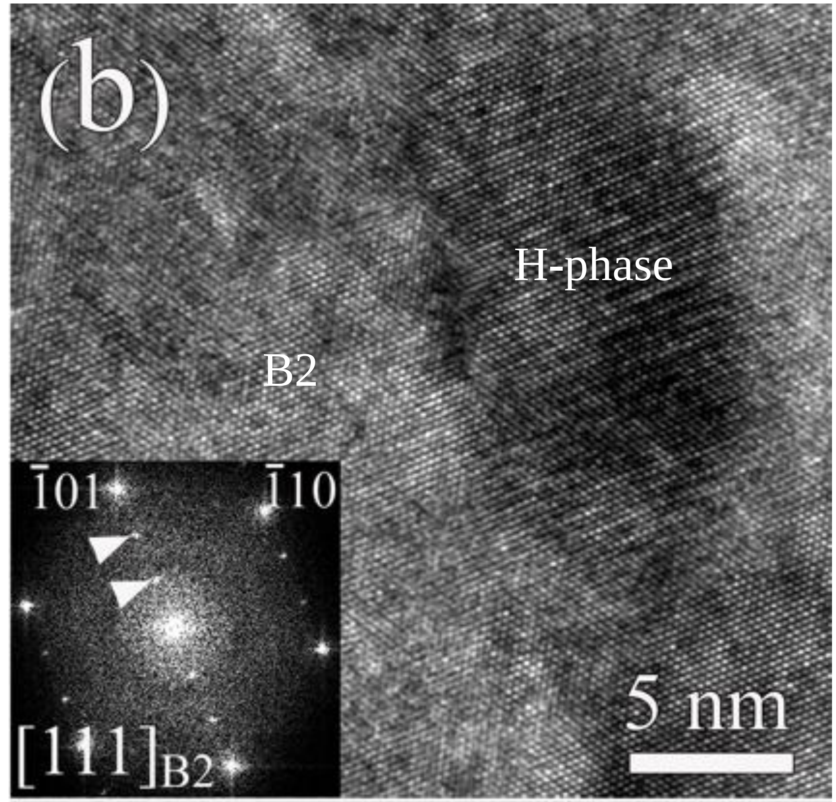
$Ni_{56}Ti_{36}Hf_8$ → SA_{WQ}



- → No Ni_4Ti_3 precipitates observed
- → Diffuse superlattice reflections corresponding to H-phase
- → Rare 2-5nm H-phase. Suppressed precipitation

$Ni_{56}Ti_{36}Hf_8$ ➔ SA_{WQ} + 550ºC $(4\ h)_{AC}$





- ➔ No Ni_4Ti_3 precipitates observed
- ➔ Dense nano-H-phase in B2 matrix
- ➔ Large heterogeneous islands (0.4-0.6 µm)

$Ni_{56}Ti_{36}Hf_8$ ➔ SHT_{WQ} + 300ºC (12 h)$_{AC}$ + 550ºC (4 h)$_{AC}$
Highest hardness

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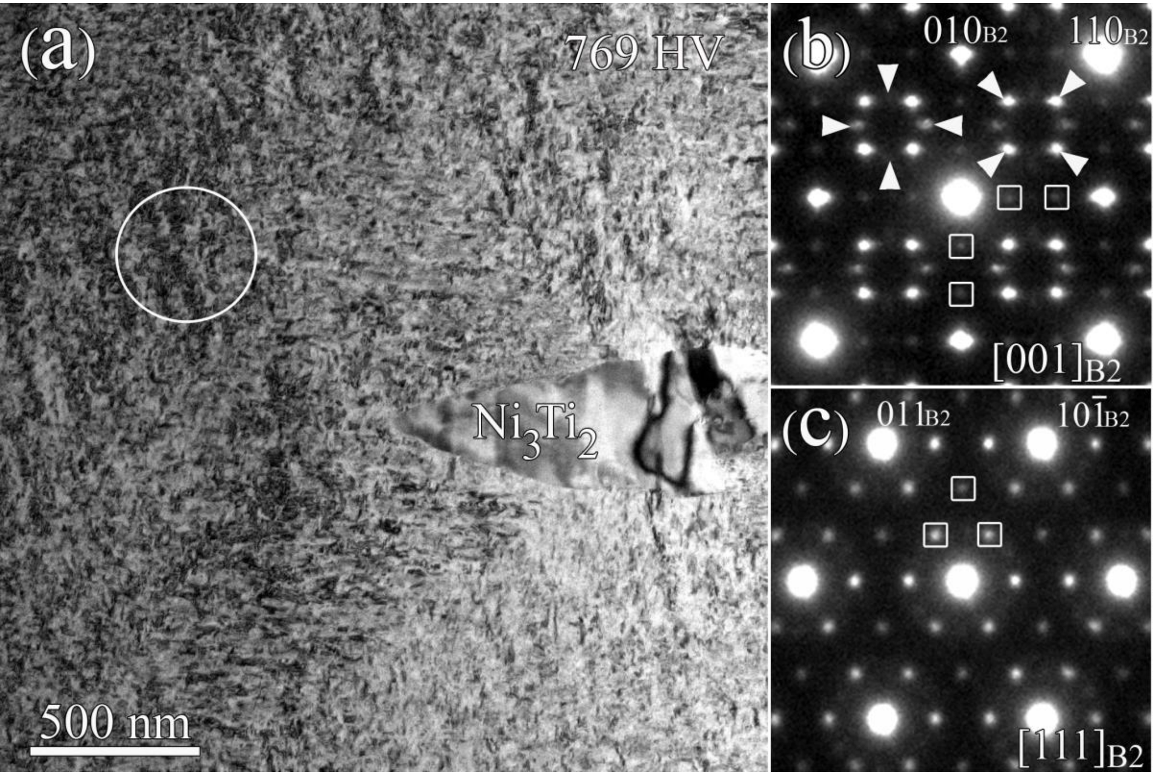

- ➔ No Ni_4Ti_3 precipitation
- ➔ Unique superlattice reflections that do not belong to Ni_4Ti_3 or H-phase
- ➔ Dense nano-H-phase <u>and</u> another secondary precipitate (Ni_3Ti_2)

Known Ni_3Ti_2 precipitation in NiTi-alloys

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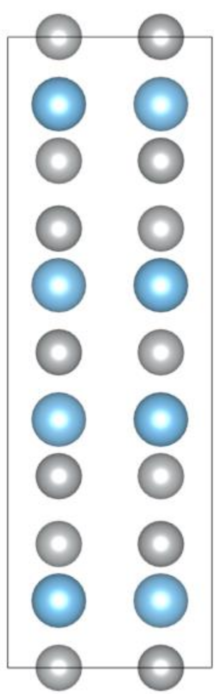
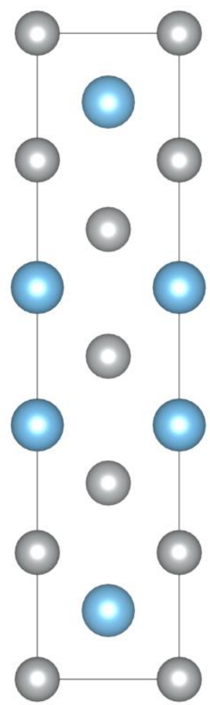
Low temperature (298K)
Orthorhombic
bbmm [63]

a=4.4Å
a=4.4Å
c=13.4Å
α=90º
β=90º
γ=90º



High temperature (373K)
Tetragonal
I4/mmm [139]

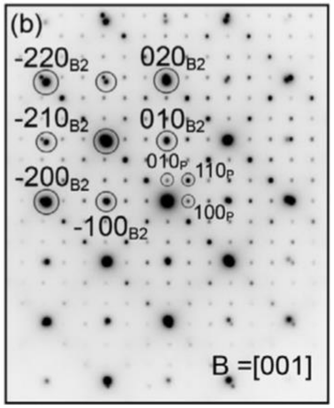
a=3.1Å
a=3.1Å
c=14.3Å
α=90º
β=90º
γ=90º

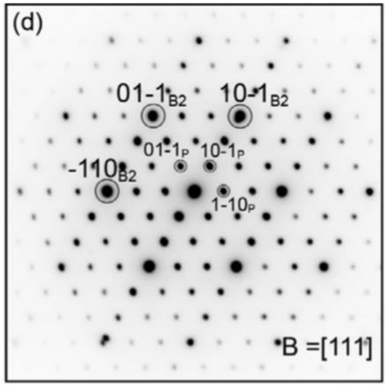


Nishida et al. (1997)

Metastable cubic
Ni_3Ti_2 in $Ni_{52}Ti_{48}$

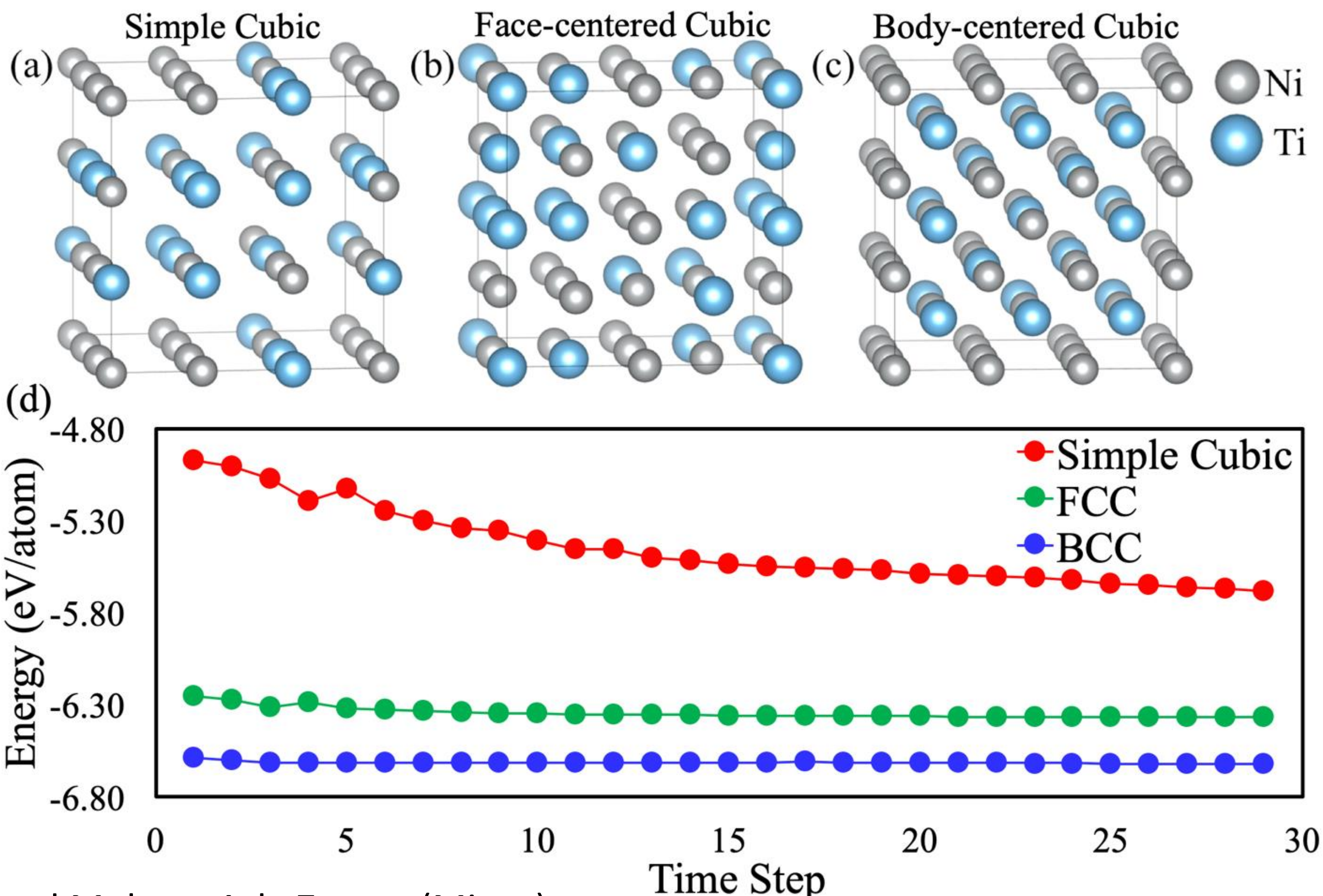
a = 8.74Å
α=90º
β=90º
γ=90º





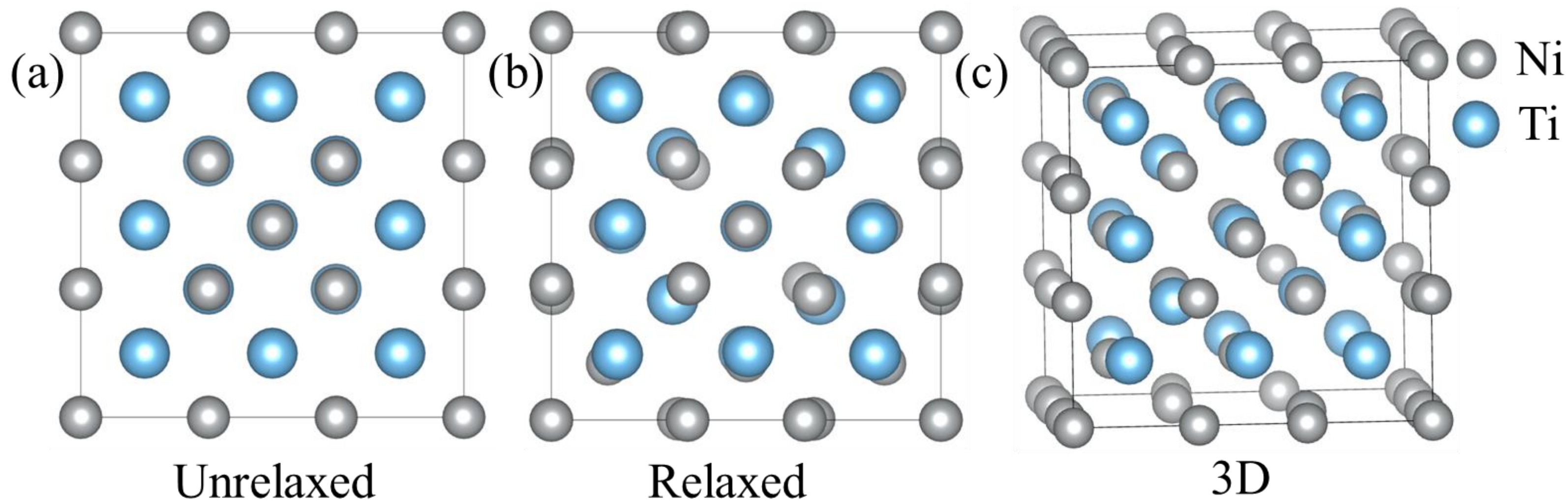
Karlík et al. (2017)

Stable structure of cubic Ni_3Ti_2 (DFT)



Yu Hong and Mohsen Asle Zaeem (Mines)

Stable structure of cubic Ni_3Ti_2 (DFT)



$Ni_{33}Ti_{21}$ Cubic crystal
Space Group: P-42m (No. 111)
Lattice parameter: a = 8.816Å
Hardness: ~830HV

Table. 1 Full description of atomic position of the proposed structure of precipitate.

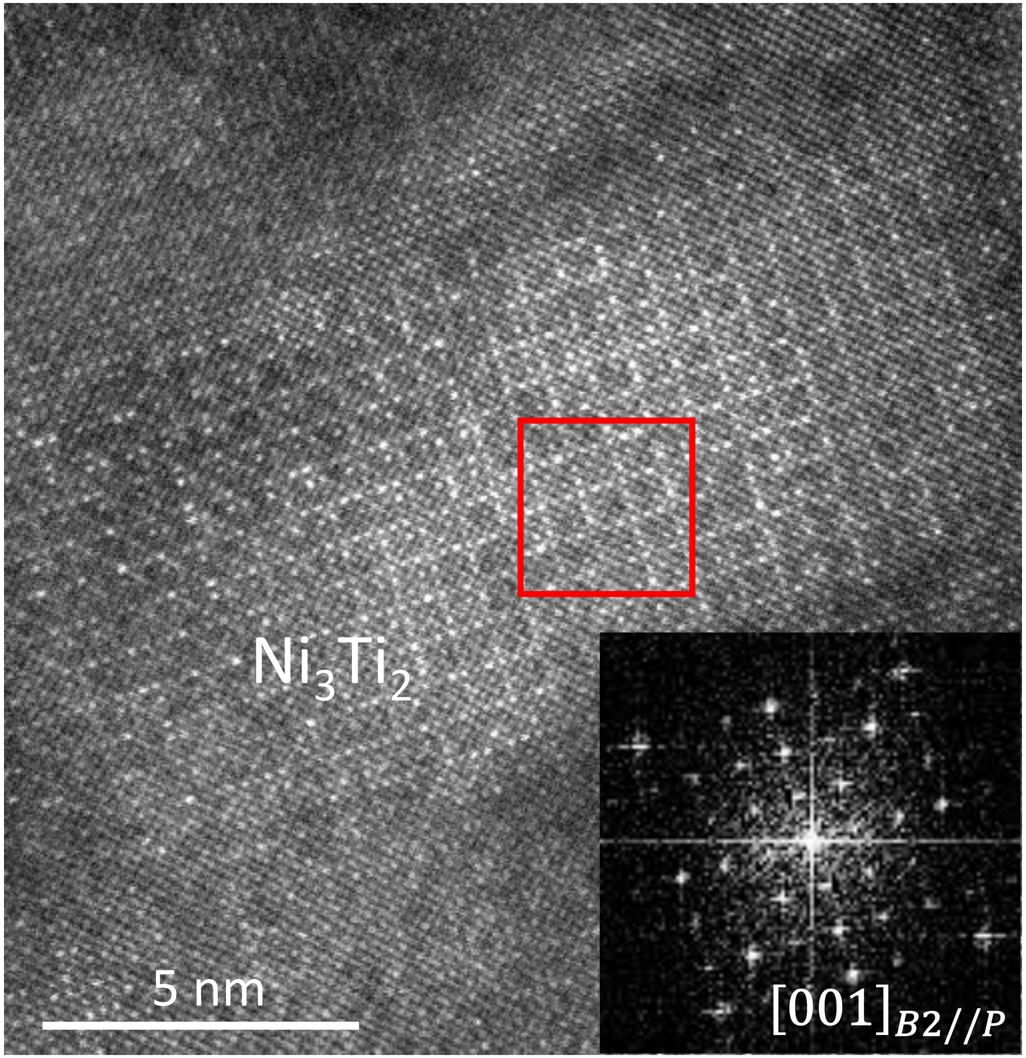
Atoms		W	M	Unrelaxed			relaxed		
				X	y	z	x	y	z
1	Ni1	a	1	0.000	0.000	0.000	0.000	0.000	0.000
2	Ni2	i	4	0.667	0.000	0.000	0.650	0.000	0.000
3	Ni3	g	2	0.000	0.000	0.667	0.000	0.000	0.694
4	Ni4	o	8	0.667	0.000	0.667	0.673	0.003	0.665
5	Ni5	n	4	0.667	0.667	0.000	0.648	0.648	0.994
6	Ni6	n	4	0.667	0.667	0.333	0.675	0.675	0.342
7	Ni7	n	4	0.167	0.167	0.500	0.145	0.145	0.497
8	Ni8	j	4	0.167	0.500	0.500	0.153	0.500	0.500
9	Ni9	h	2	0.500	0.500	0.833	0.500	0.500	0.800
10	Ti1	n	4	0.833	0.833	0.167	0.832	0.832	0.173
11	Ti2	o	8	0.500	0.167	0.833	0.505	0.177	0.824
12	Ti3	n	4	0.167	0.167	0.833	0.169	0.169	0.841
13	Ti4	n	4	0.667	0.667	0.667	0.689	0.689	0.621
14	Ti5	b	1	0.500	0.500	0.500	0.500	0.500	0.500

$Ni_{33}Ti_{21}$: Cubic crystal, space group *P-42m* (No. 111) (a = 8.816 Å)

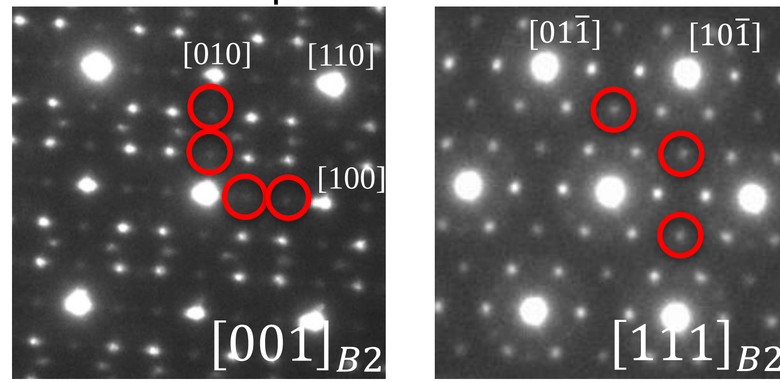
Yu Hong and Mohsen Asle Zaeem (Mines)

Stable structure of cubic Ni_3Ti_2

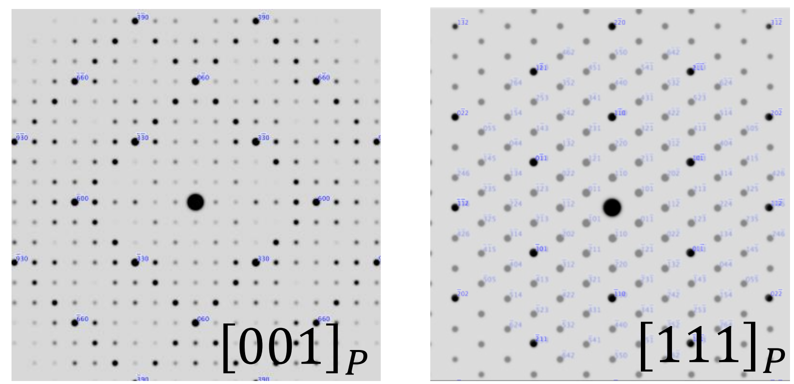
Atomic resolution STEM



Experimental SAED

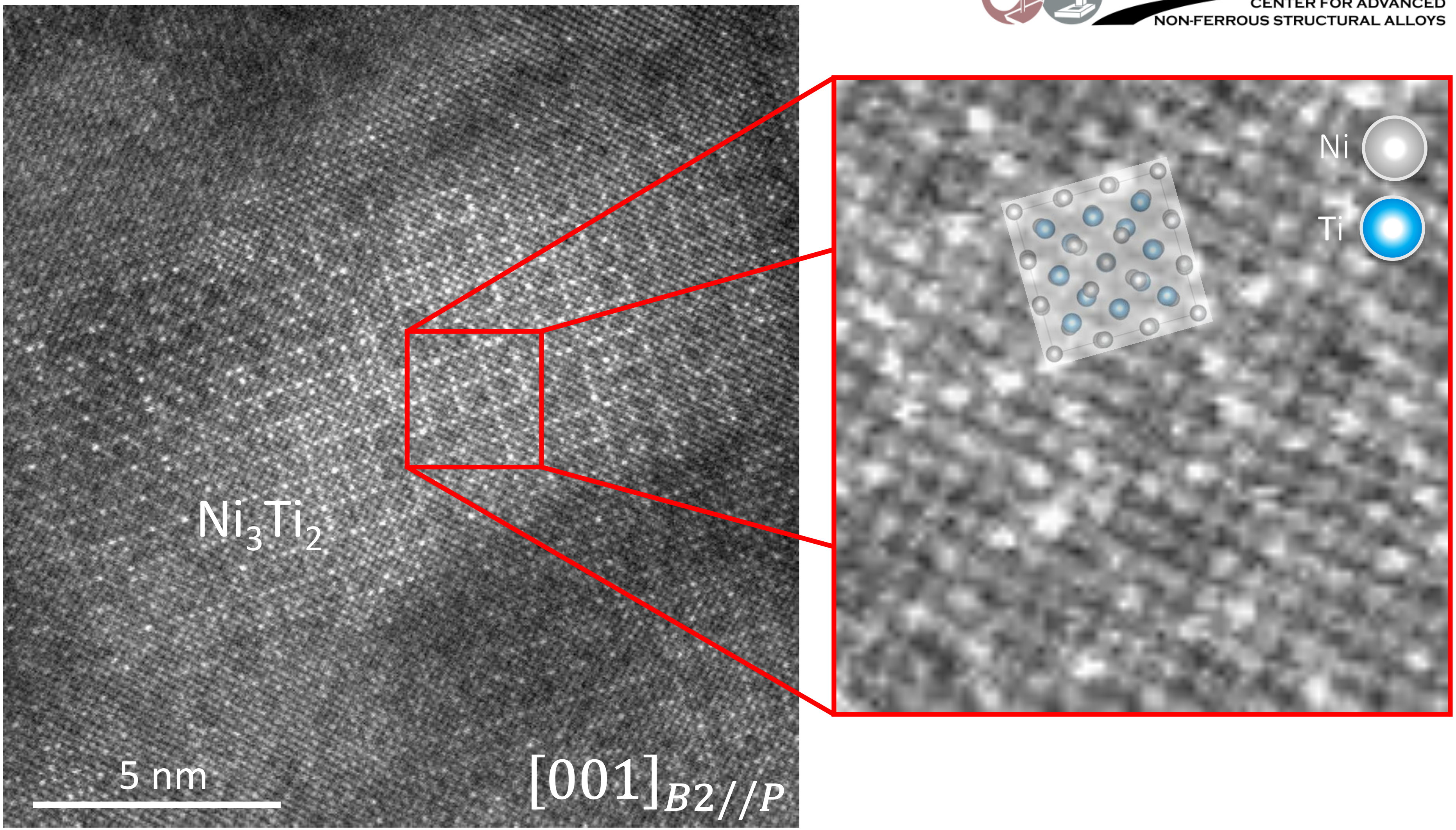


Simulated SAED



Stable structure of cubic Ni_3Ti_2

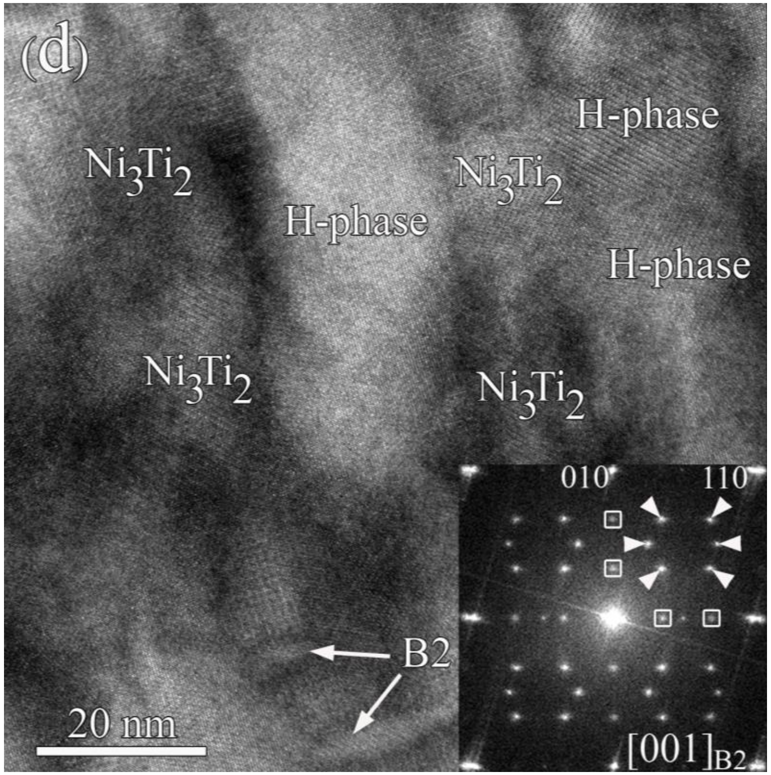
Atomic resolution STEM



➔ Atomic columns at the edge positions of the unit cell (Ni) are higher intensity than center positions (Ni + Ti)

Highest hardness observed for $Ni_{56}Ti_{36}Hf_8$ due to…

…mottled microstructure containing H-phase and cubic Ni_3Ti_2 with narrow B2 channels!



What happens to the microstructure after fatigue deformation?

FIB lift-out samples made from RCF wear-tracks for 2 conditions

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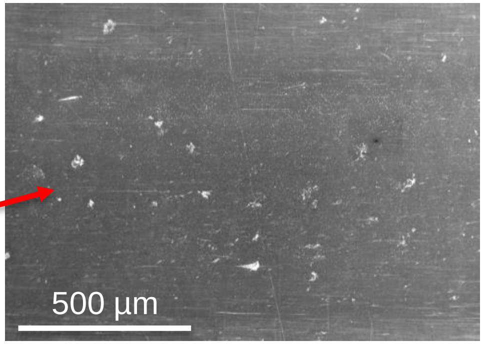
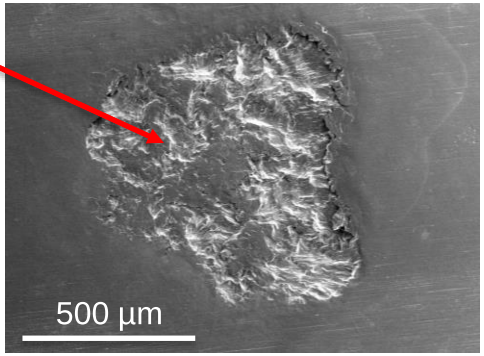
Used RCF rod

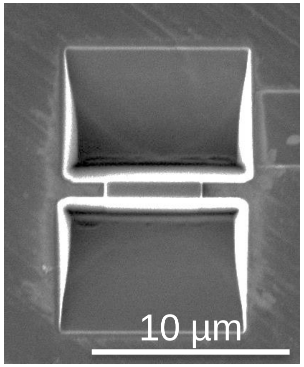
2• Runout (rolling contact fatigue)

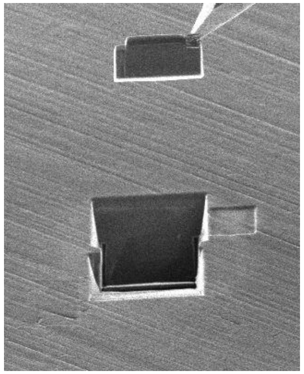


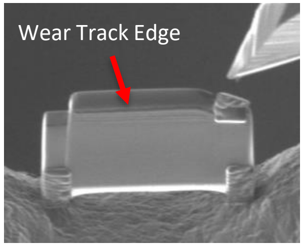
3• Spall (surface failure)



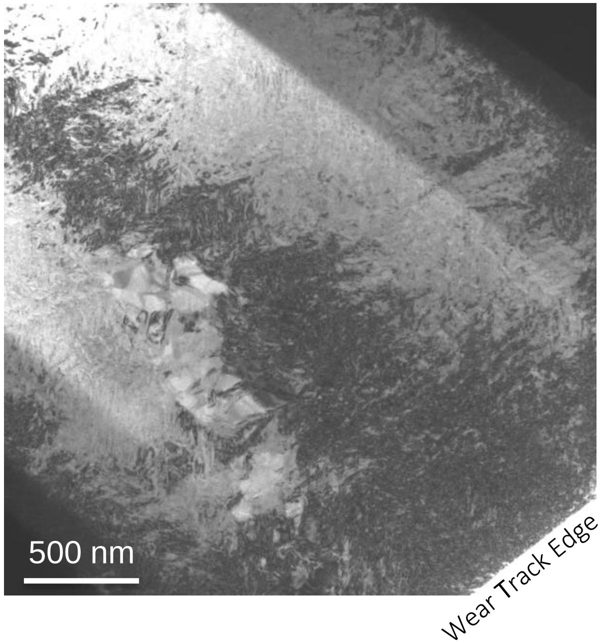
FIB foils taken directly from wear surface



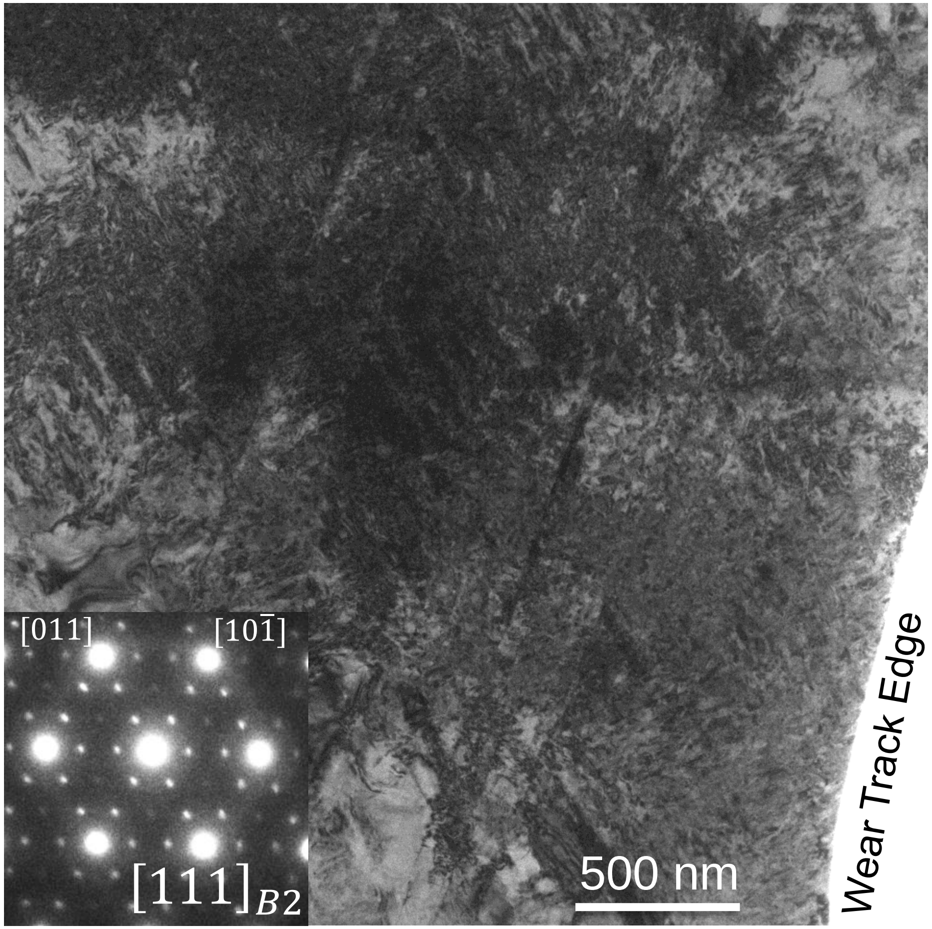


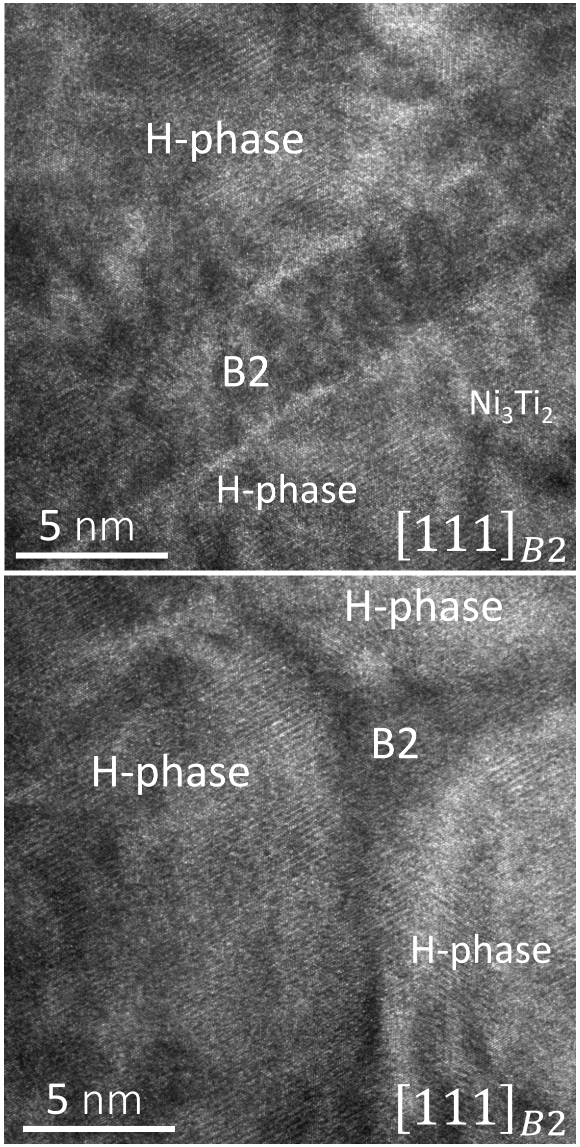


BF-TEM and HR-TEM analysis of subsurface deformation



RCF runout $Ni_{56}Ti_{36}Hf_8$ specimen (FIB)





- ➔ Fine observable bands exist under wear track
- ➔ Broadening of B2 channels
- ➔ {011} planar slip activated

RCF runout $Ni_{55}Ti_{45}$ specimen (FIB)

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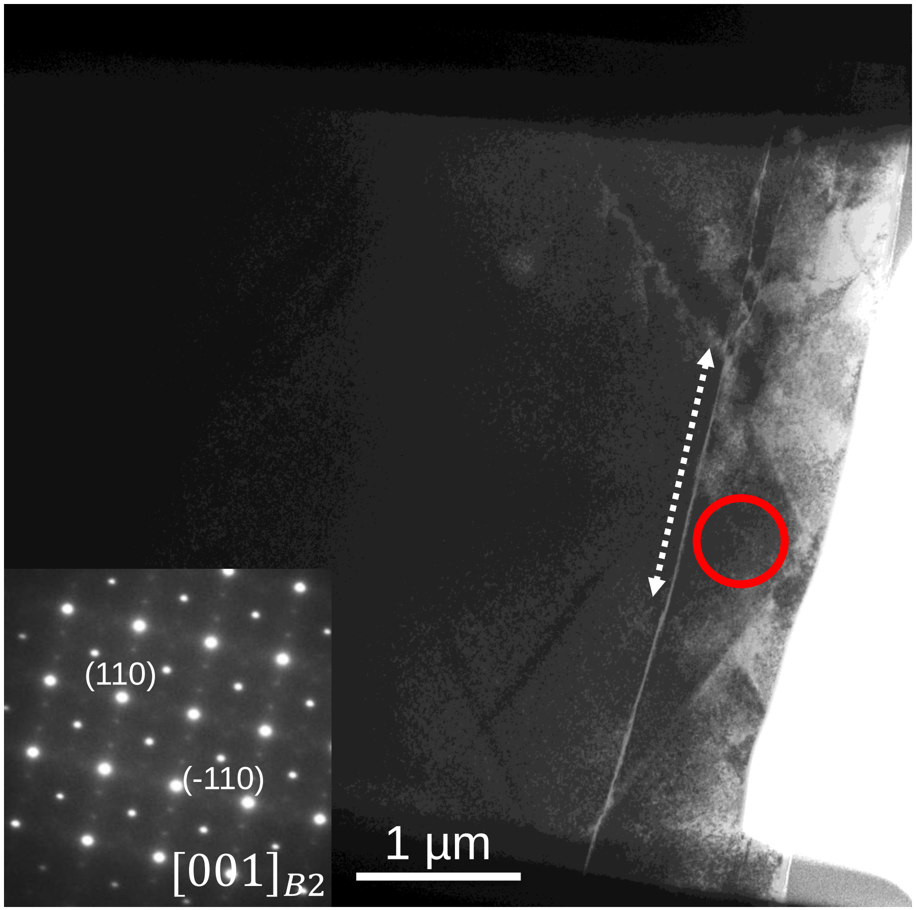

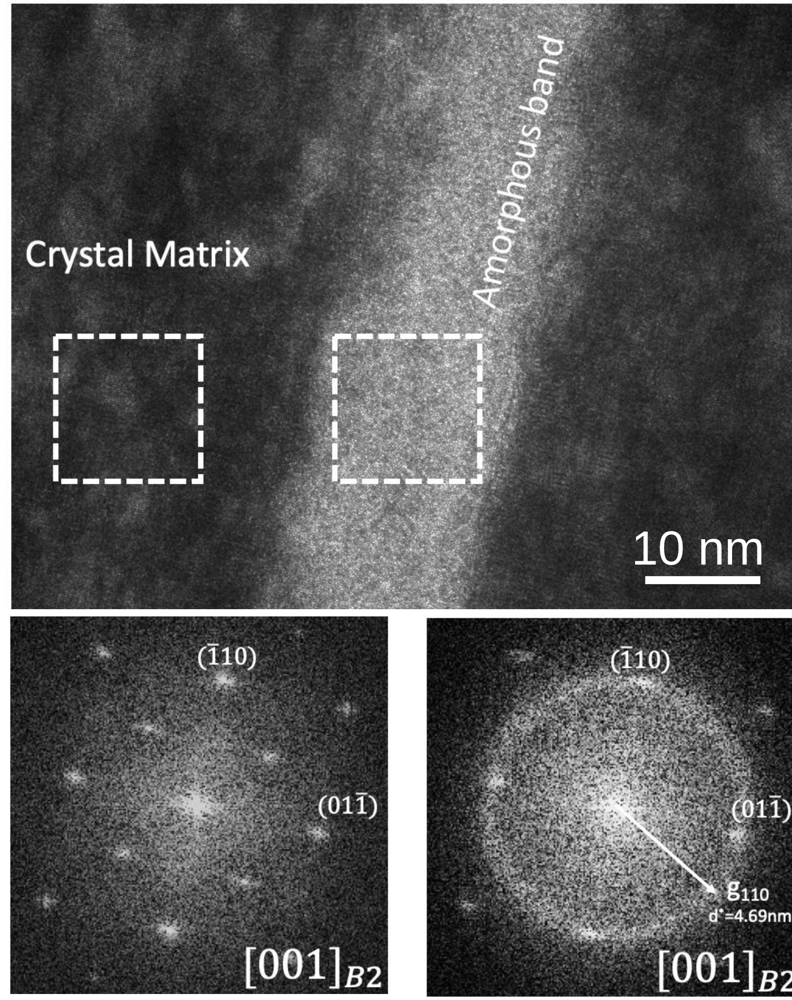

➔ Significant {011} planar slip observed

Spalled $Ni_{56}Ti_{36}Hf_8$ specimen (FIB)

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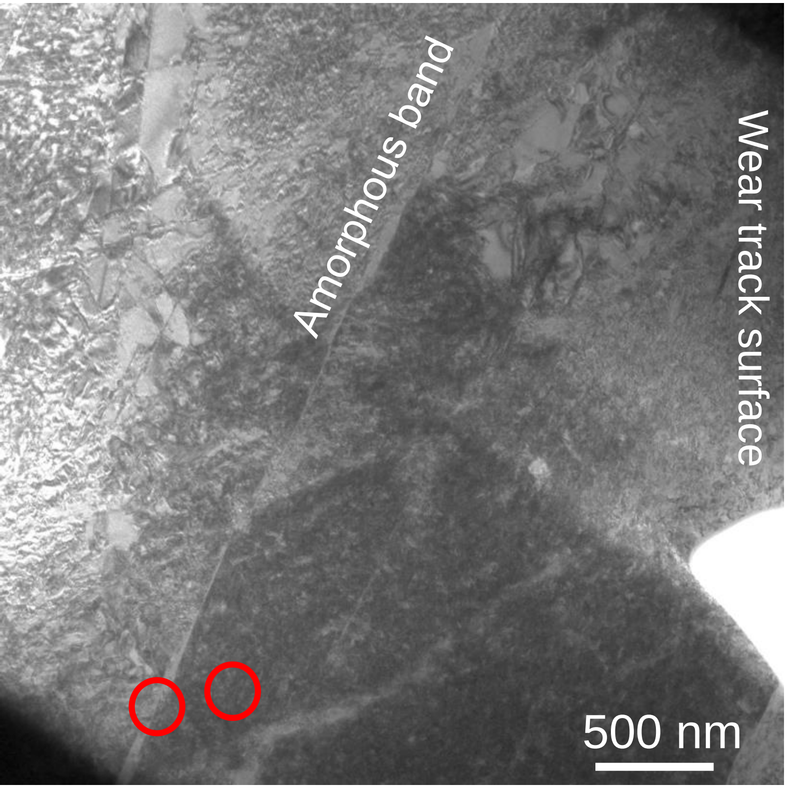
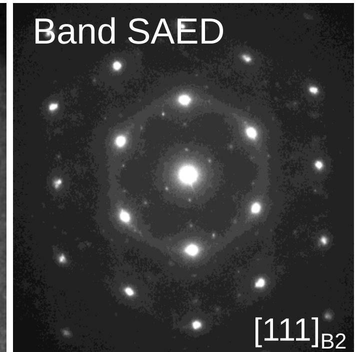
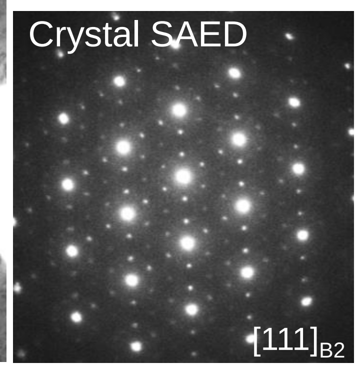
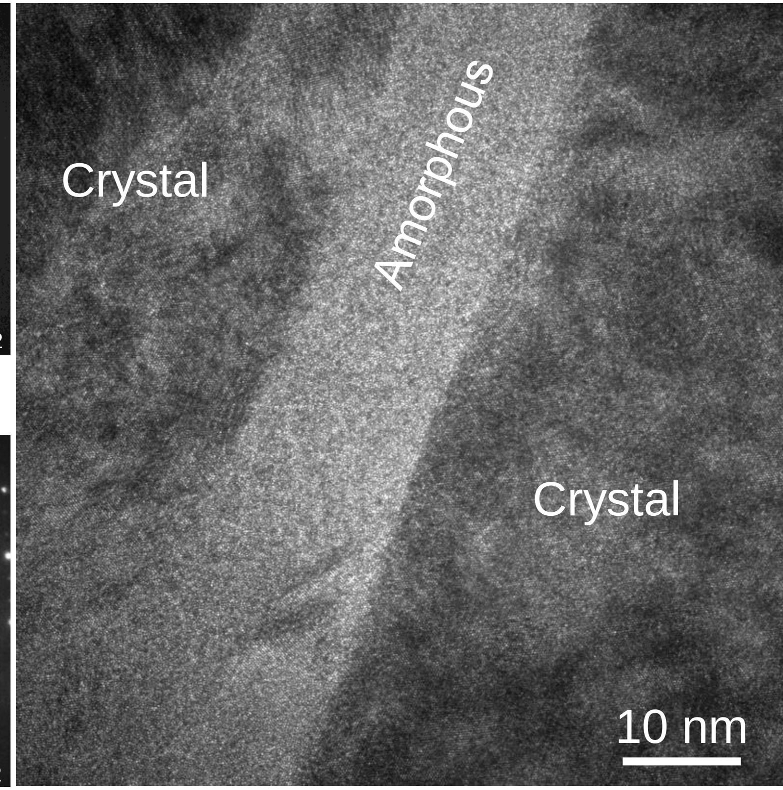
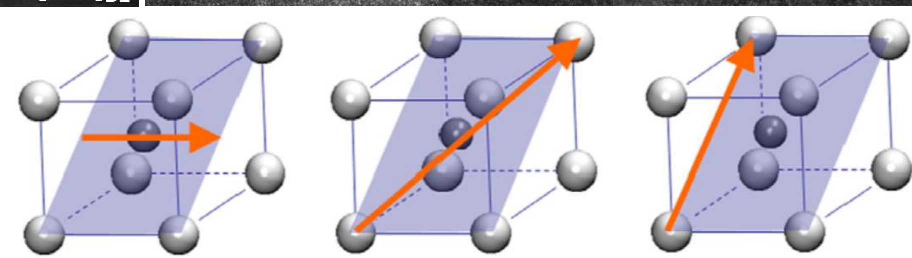








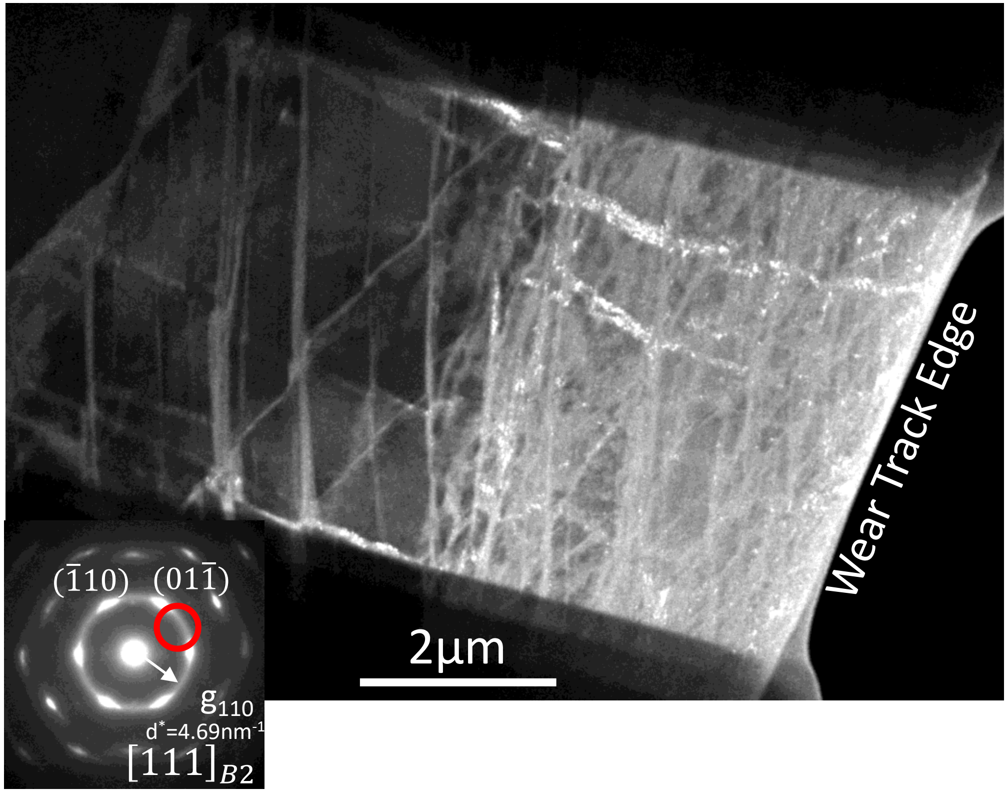
- ➔ Amorphous band has formed on {011}.
- ➔ Connection to B2 bands observed in runout specimen.



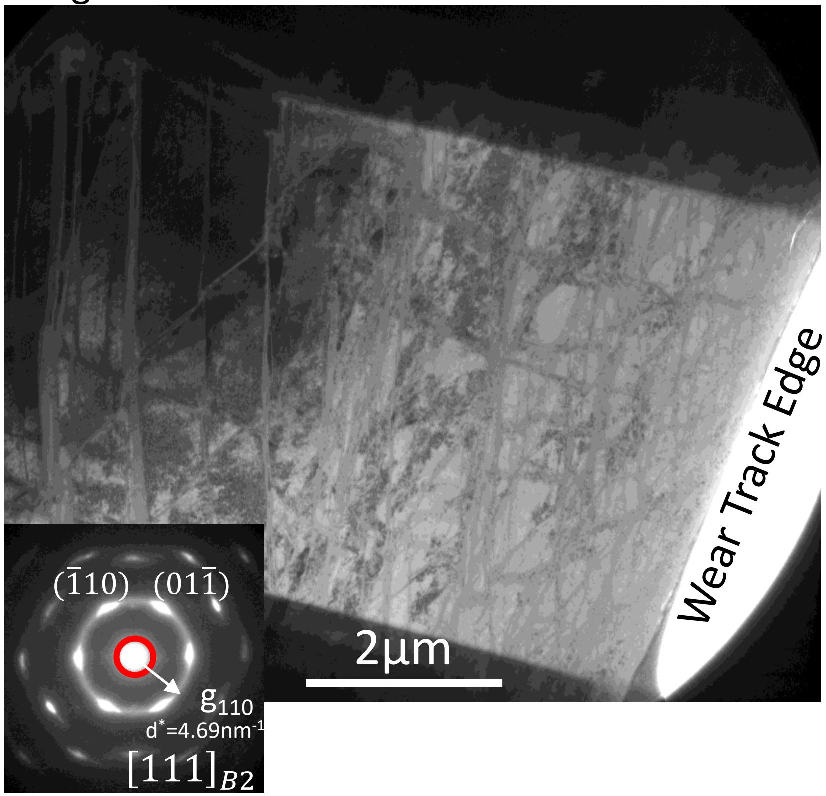
Ezaz 2013

Spalled $Ni_{55}Ti_{45}$ specimen (FIB)

Dark Field



Bright Field



➔Heavy amorphization ~5µm from edge of wear track

➔ Martensitic grain ~10µm from wear track

Spalled $Ni_{55}Ti_{45}$ specimen (FIB)

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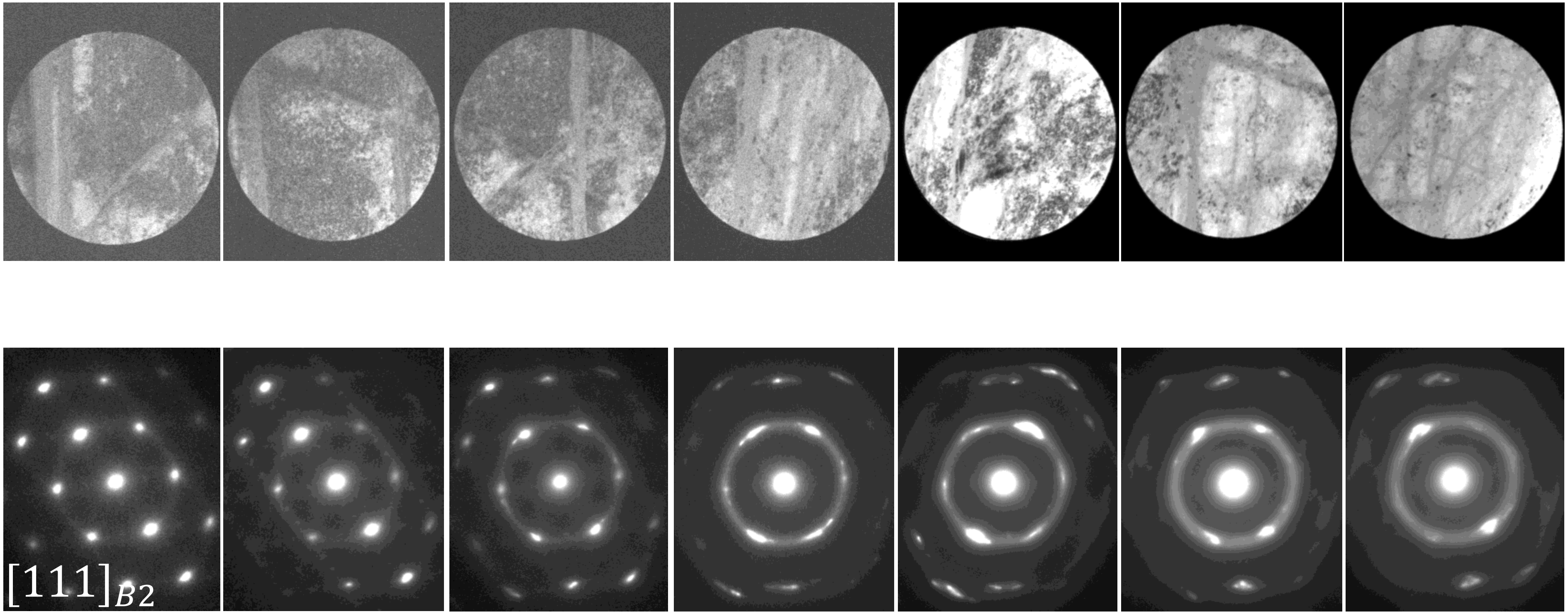

Interior of sample ← Edge of sample

➔ Gradient of deformation from edge of spall to sample interior

Conclusions and future work for Ni-Ti-Hf

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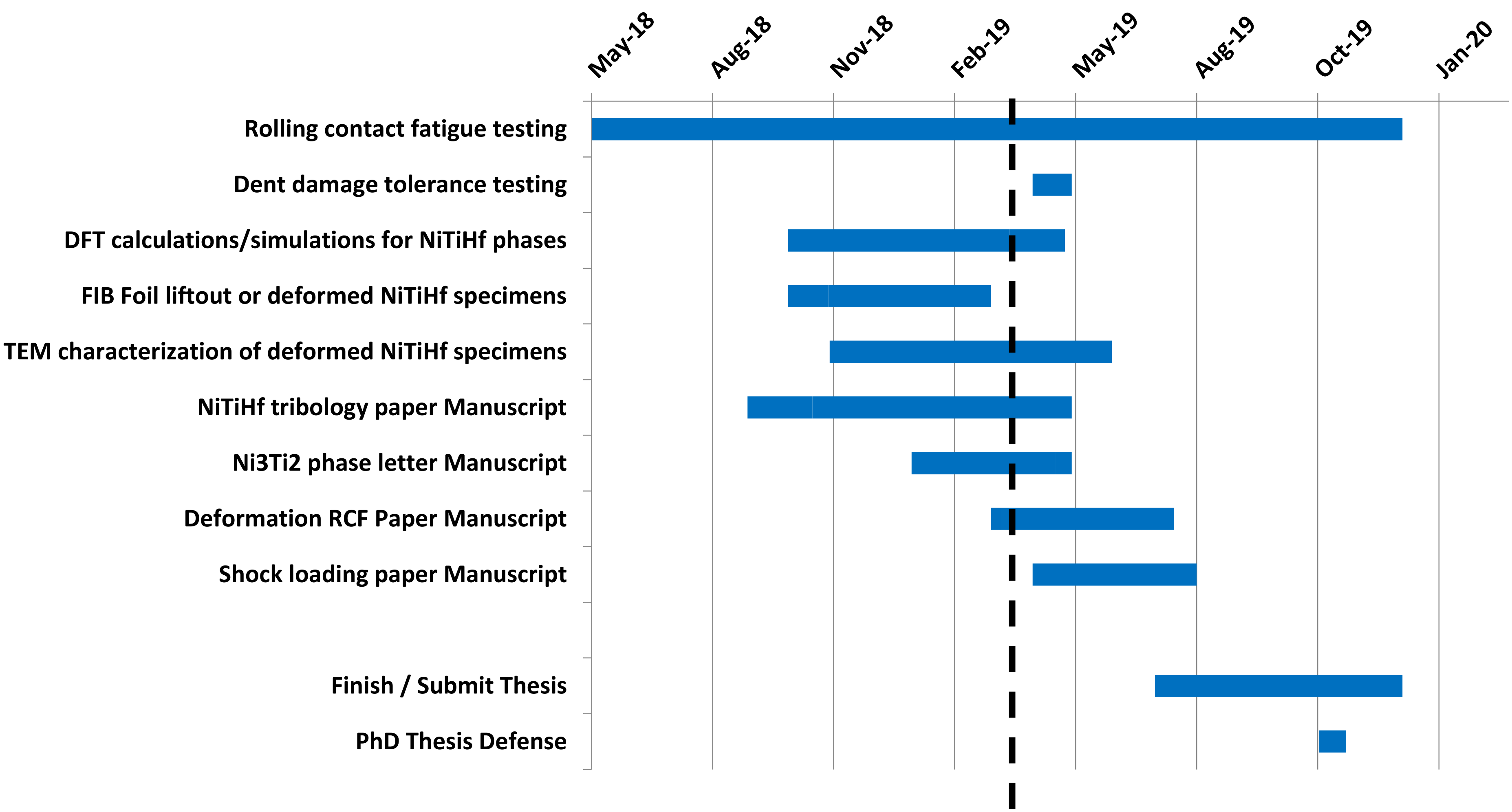
- ➔ Homogenous nano-scale H-phase and cubic Ni_3Ti_2 precipitation strengthening leads to enhanced structural properties.
- ➔ Cubic Ni_3Ti_2 is confirmed to be stable via DFT simulations and experimental findings.
- ➔ Tribology on optimized 56 at.% NiTiHf compositions shows modest increase in fatigue stress limit at 2.0 – 2.1 GPa.
- ➔ B2 channels transform to B2 bands under $Ni_{56}Ti_{36}Hf_8$ wear track during fatigue and finally become amorphous under spall.
- ➔ More observed slip traces activated in fatigued $Ni_{55}Ti_{45}$ specimen. Spalled $Ni_{55}Ti_{45}$ specimen is heavily amorphized up to 5µm away from wear track edge.

Progress


May-18
Aug-18
Nov-18
Feb-19
May-19
Aug-19
Oct-19
Jan-20
Rolling contact fatigue testing
Dent damage tolerance testing
DFT calculations/simulations for NiTiHf phases
FIB Foil liftout or deformed NiTiHf specimens
TEM characterization of deformed NiTiHf specimens
NiTiHf tribology paper Manuscript
Ni3Ti2 phase letter Manuscript
Deformation RCF Paper Manuscript
Shock loading paper Manuscript
Finish / Submit Thesis
PhD Thesis Defense

Thank you very much!

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Ronald Noebe (NASA GRC)

Sean Mills
Colorado School of Mines
seanmills@mines.edu
Stebnerlab.mines.edu

Center for Electron Microscopy and Analysis

Project 17 – Nickel-Titanium-Hafnium alloy design for tribological systems

Student: *Sean MIlls*

Faculty: *Aaron Stebner*

Industrial Partners: *NASA GRC (Ron Noebe, Chris Dellacorte)*

Project Duration: *Aug. 2015 – Aug. 2019*

Achievement

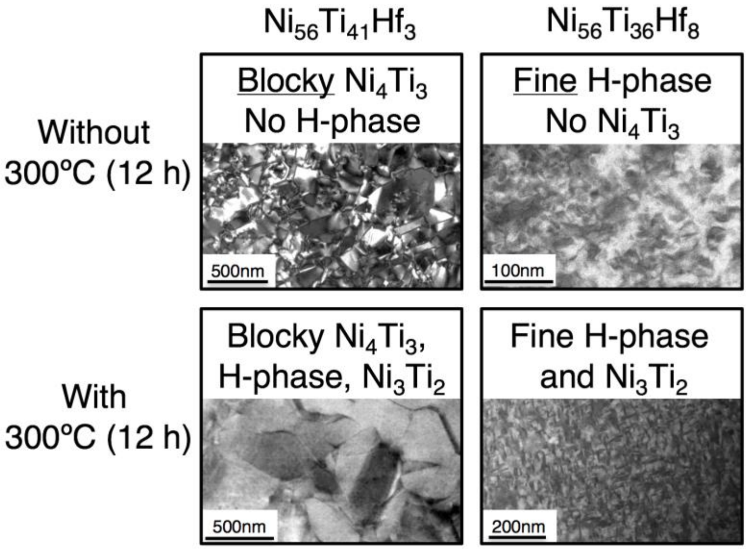
- Novel Ni-rich alloys provide ultra-hard optimized microstructures designed for space-age tribology applications.

Significance and Impact

- Hf-alloying could lead to reduction in residual stress by eliminating the need for rapid cooling while retaining high strength and hardness levels of quenched binary Ni-Ti.

Research Details

- Rolling contact fatigue testing and microstructure characterization of Ni-rich NiTiHf alloys.



Quantitative data from TEM study

Composition / HT	Ni_4Ti_3 Length (nm)	Ni_4Ti_3 Width (nm)	Ni_4Ti_3 distance (nm)	H-Phase Length (nm)	H-Phase Width (nm)	H-Phase distance (nm)	Hardness (HV)
$Ni_{56}Ti_{41}Hf_3$ / WQ	63 ± 16	63 ± 16	42 ± 13	**	**	**	707 ± 9
$Ni_{56}Ti_{41}Hf_3$ / WQ + 550(4 h)	113 ± 32	87 ± 19	92 ± 24	**	**	**	682 ± 10
$Ni_{56}Ti_{41}Hf_3$ / WQ + 300(12 h)	65 ± 21	65 ± 21	51 ± 19	**	**	**	752 ± 7
$Ni_{56}Ti_{41}Hf_3$ / WQ + 300(12 h) + 550(4 h)	138 ± 41	94 ± 23	105 ± 33	28 ± 4	13 ± 2	104 ± 13	710 ± 2
$Ni_{56}Ti_{36}Hf_8$ / WQ	**	**	**	2 - 5	2 - 5	??	716 ± 4
$Ni_{56}Ti_{36}Hf_8$ / WQ + 550(4 h)	**	**	**	21 ± 6	8 ± 2	17 ± 6	700 ± 7
$Ni_{56}Ti_{36}Hf_8$ / WQ + 300(12 h)	**	**	**	2 - 5	2 - 5	??	705 ± 8
$Ni_{56}Ti_{36}Hf_8$ / WQ + 300(12 h) + 550(4 h)	**	**	**	23 ± 5	12 ± 3	7 ± 2	769 ± 7

Ni-Ti-Hf application space

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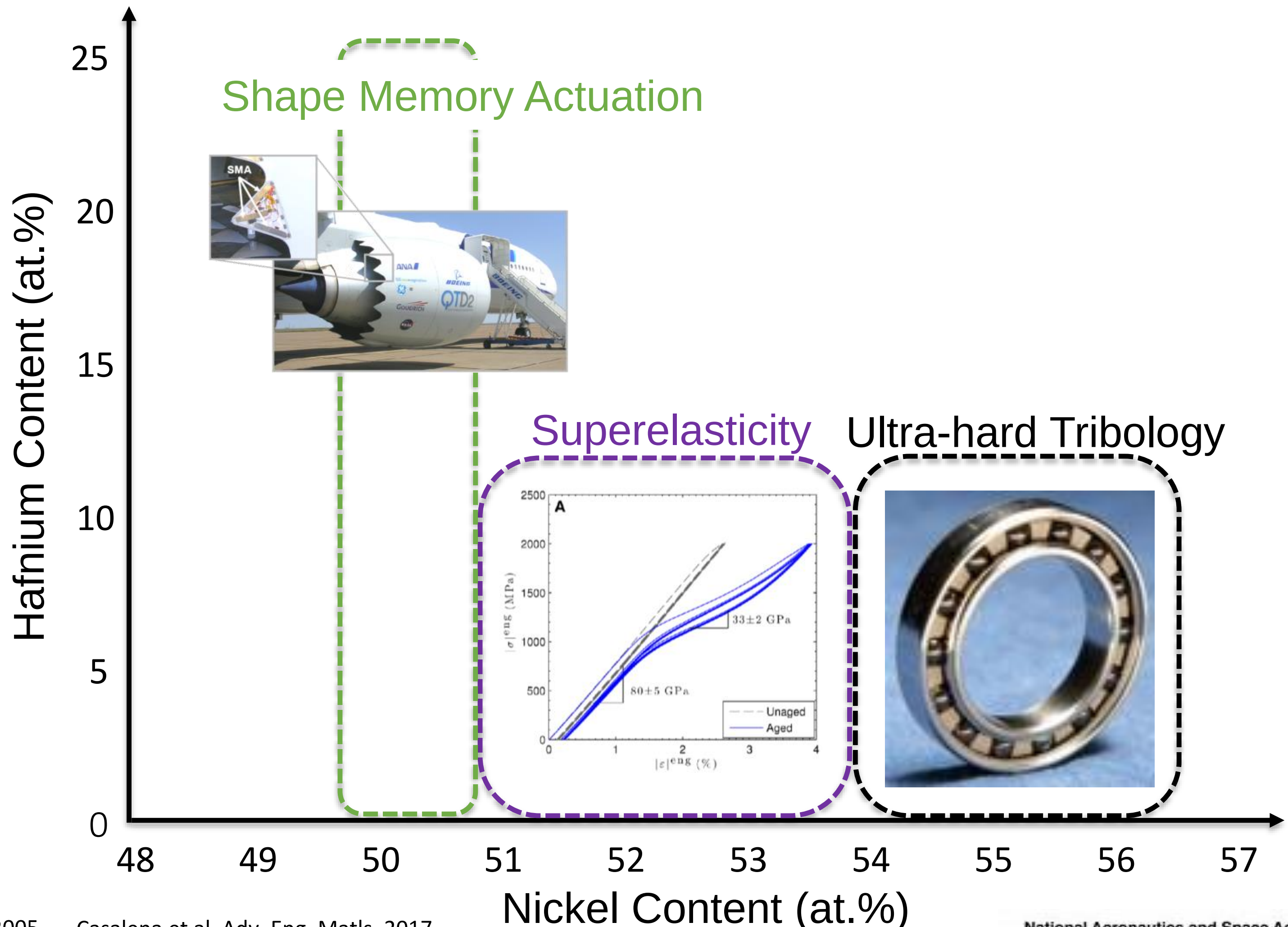


Mabe, Calkins, et al. 2005

Casalena et al. Adv. Eng. Matls. 2017

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field

Compositional stability plays an important role in precipitation

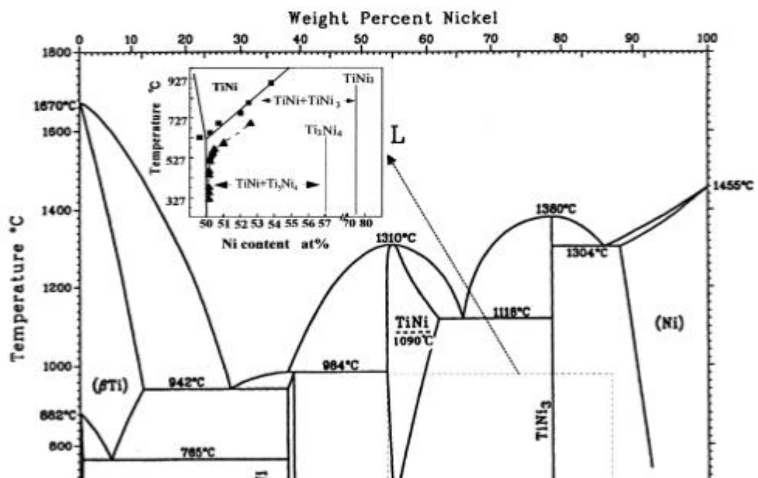
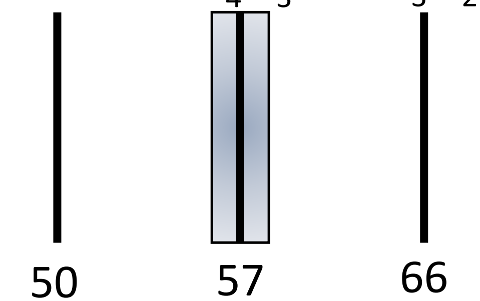


Fig. 2. Pl
and Ti3N
Research

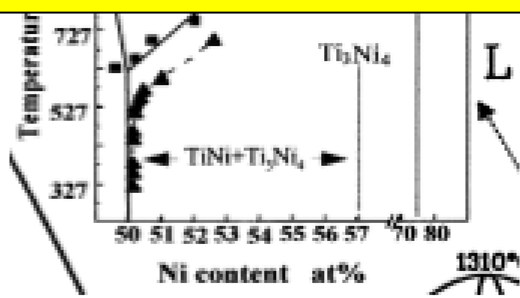
$Ni_{56}Ti_{41}Hf_3$ alloy

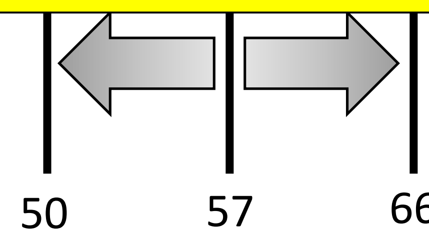
NiTi Ni_4Ti_3 Ni_3Ti_2



at.% Ni

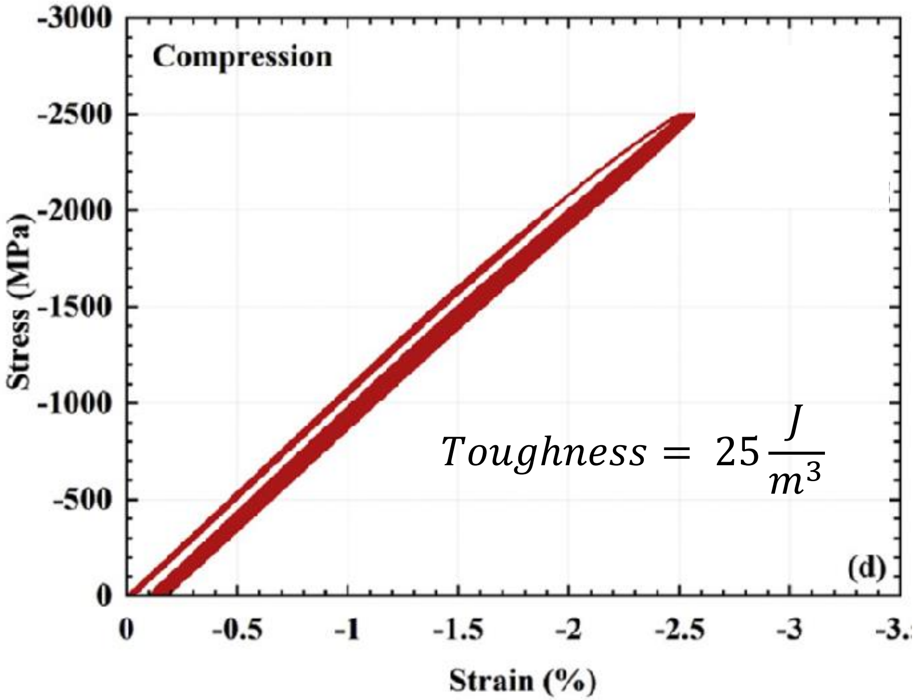
The existing binary phase diagram must be revised to accommodate complex precipitation pathways in NiTiHf alloys





Ni-Ti-Hf alloys show higher toughness exhibit large superelasticity

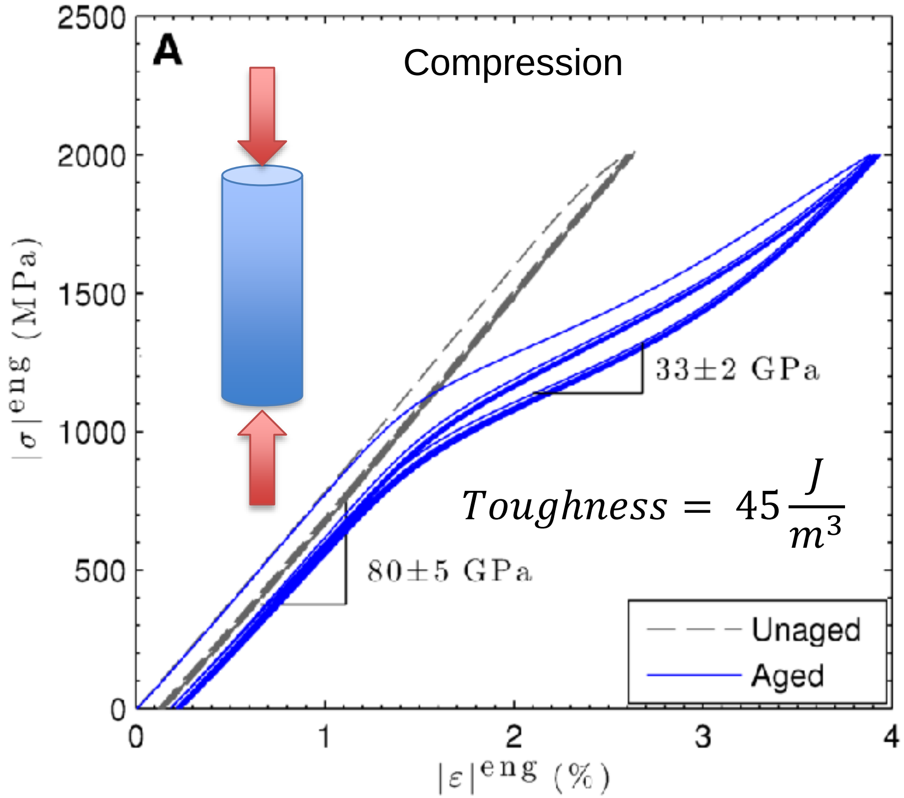
55at% NiTi in compression



$$Toughness = 25\frac{J}{m^3}$$

Benafan et al. Intermetallics 2017

$Ni_{54}Ti_{45}Hf_1$ in compression



$$Toughness = 45\frac{J}{m^3}$$

Casalena et al. Adv. Eng. Matls. 2017