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Center for Advanced Non-Ferrous Structural Alloys
An Industry/University Cooperative Research Center

Project 17: Nickel-Titanium-Hafnium Alloy Design in Tribological Systems

Fall 2018 Semi-Annual Meeting
Colorado School of Mines, Golden, CO
October 2-4, 2018

Student: Sean Mills (Mines)

Faculty: Aaron Stebner (Mines)

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

Other Participants : Behnam Aminahmadi (Mines)

Project 17: *Nickel-Titanium-Hafnium Alloy Design in Tribological Systems*

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

Project Duration
PhD: August 2015 to August 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 $Ni_{56}Ti_{41}Hf_3$ and $Ni_{56}Ti_{36}Hf_8$ alloy specimens
- TEM characterization of microstructure evolution in $Ni_{56}Ti_{36}Hf_8$
- WAXS-based Time/Temperature/Transformation (TTT) research

Metrics

Description	% Complete	Status
1. Residual stress and hardness testing on $Ni_{55}Ti_{45}$ & $Ni_{54}Ti_{45}Hf_1$ (NASA)	80%	●
2. Literature review	85%	●
3. Rolling contact fatigue characterization of $Ni_{54}Ti_{45}Hf_1$ alloy	80%	●
4. Time/Temperature/Transformation of $Ni_{54}Ti_{45}Hf_1$ alloy	40%	●
5. Alloy optimization – vary nickel and hafnium contents by 1-8 at%	40%	●

Industrial relevance

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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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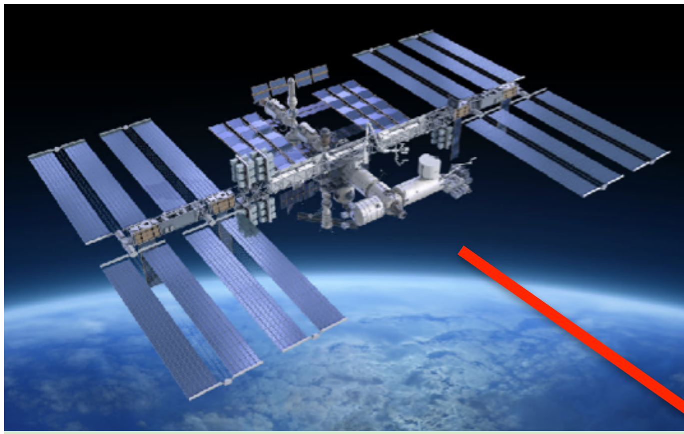
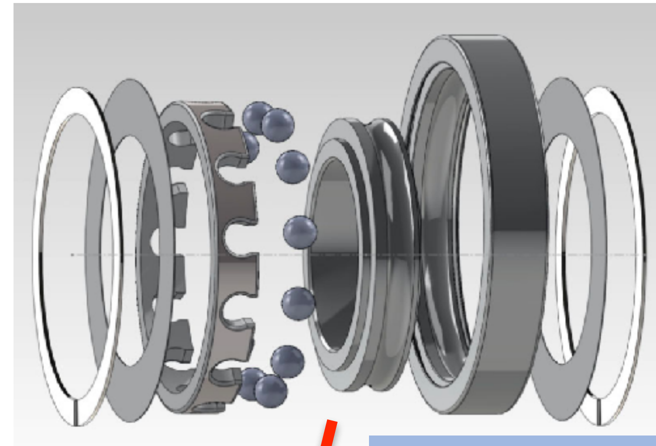
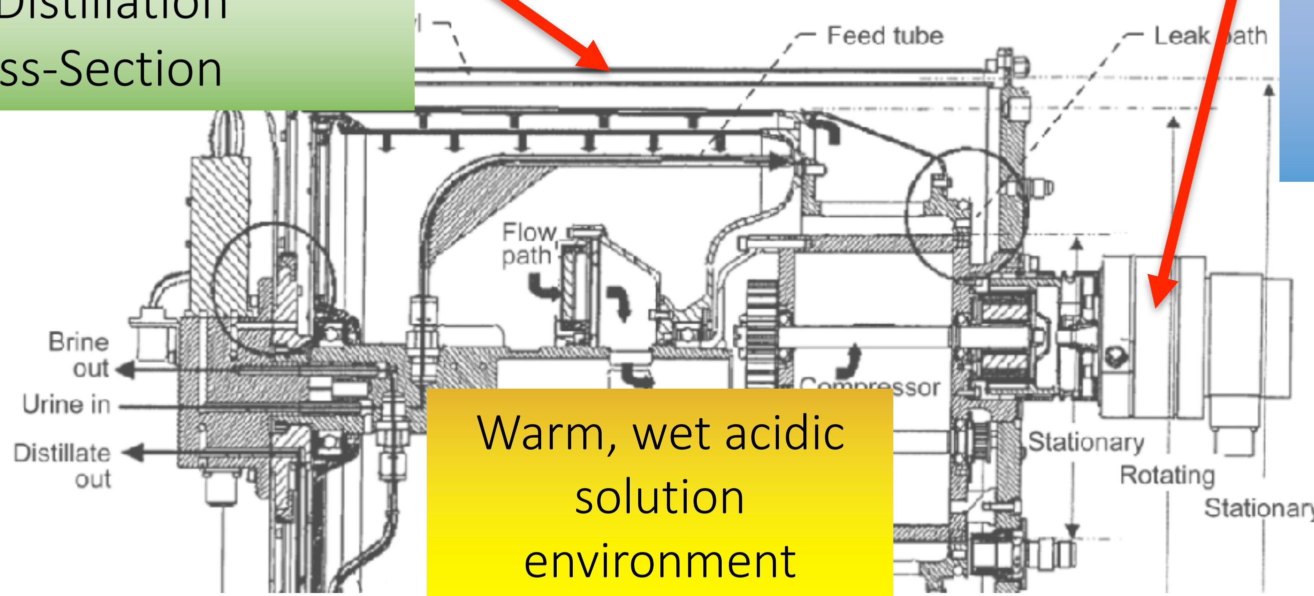


ISS Distillation Cross-Section



Rotating Centrifuge Bearing



Warm, wet acidic solution environment

Dellacorte et al.
NASA/TM 2012

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

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Nickel-rich Ni-Ti alloy shows superior damage resistance

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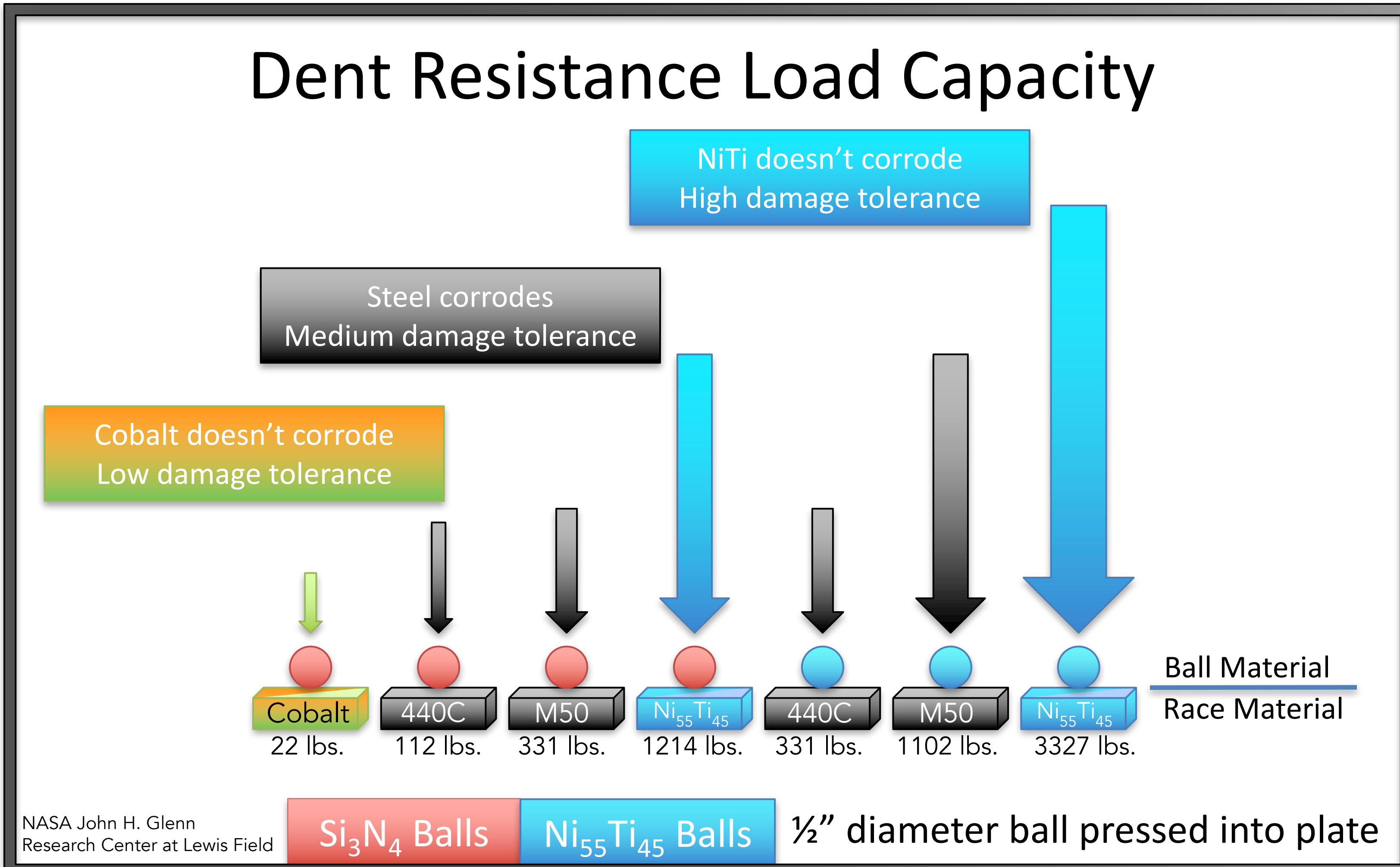

Ni-Ti has better corrosion resistance than steel

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

Binary Ni-Ti bearing races are susceptible to untimely failures

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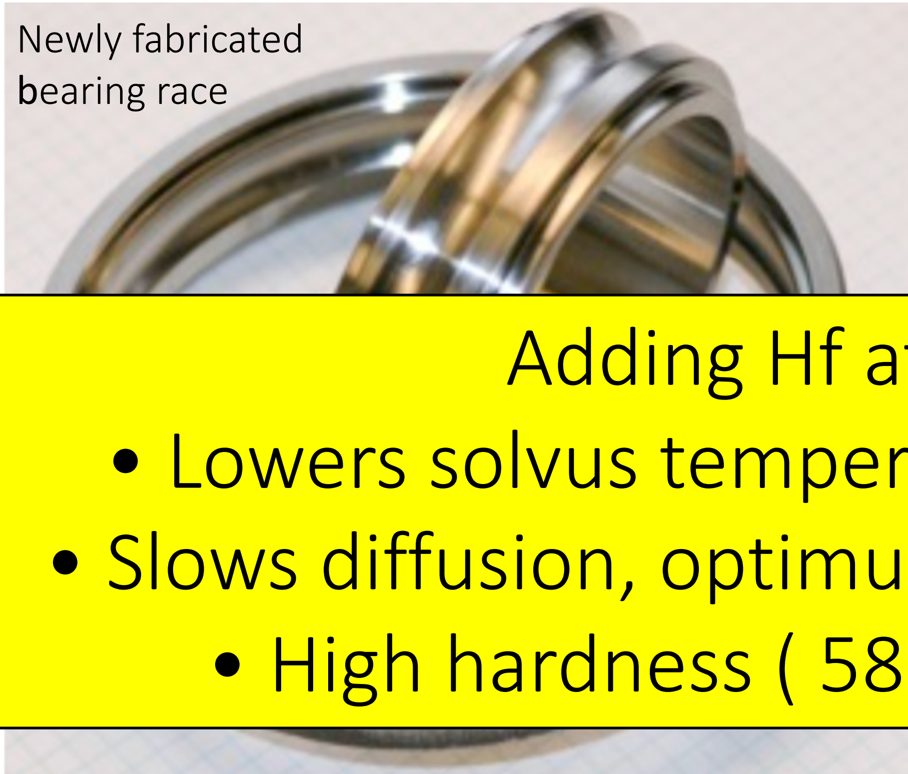
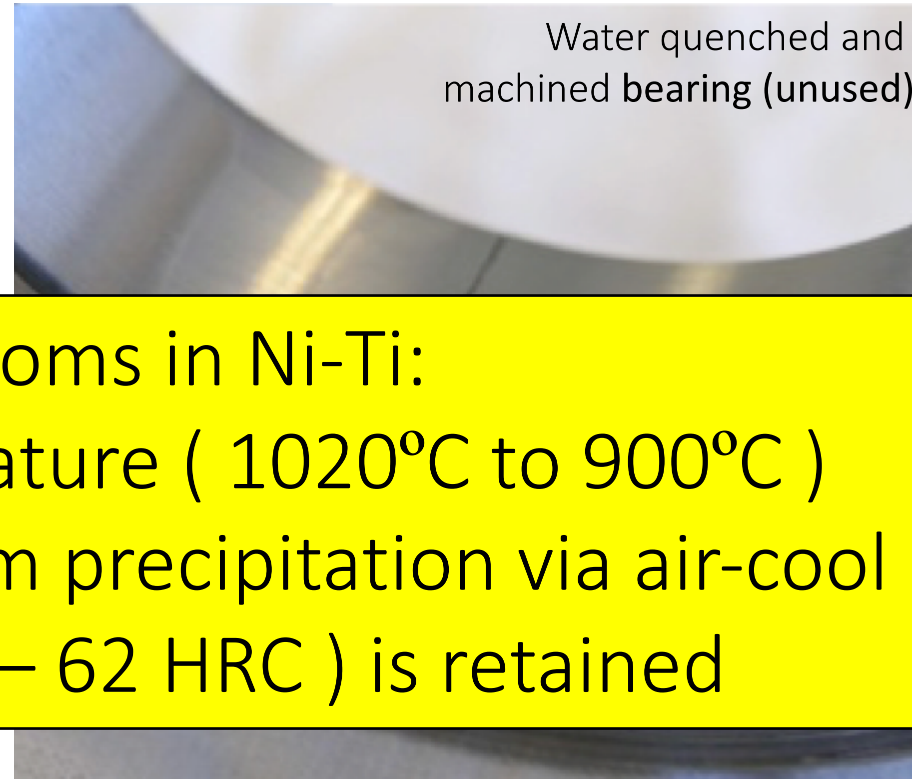




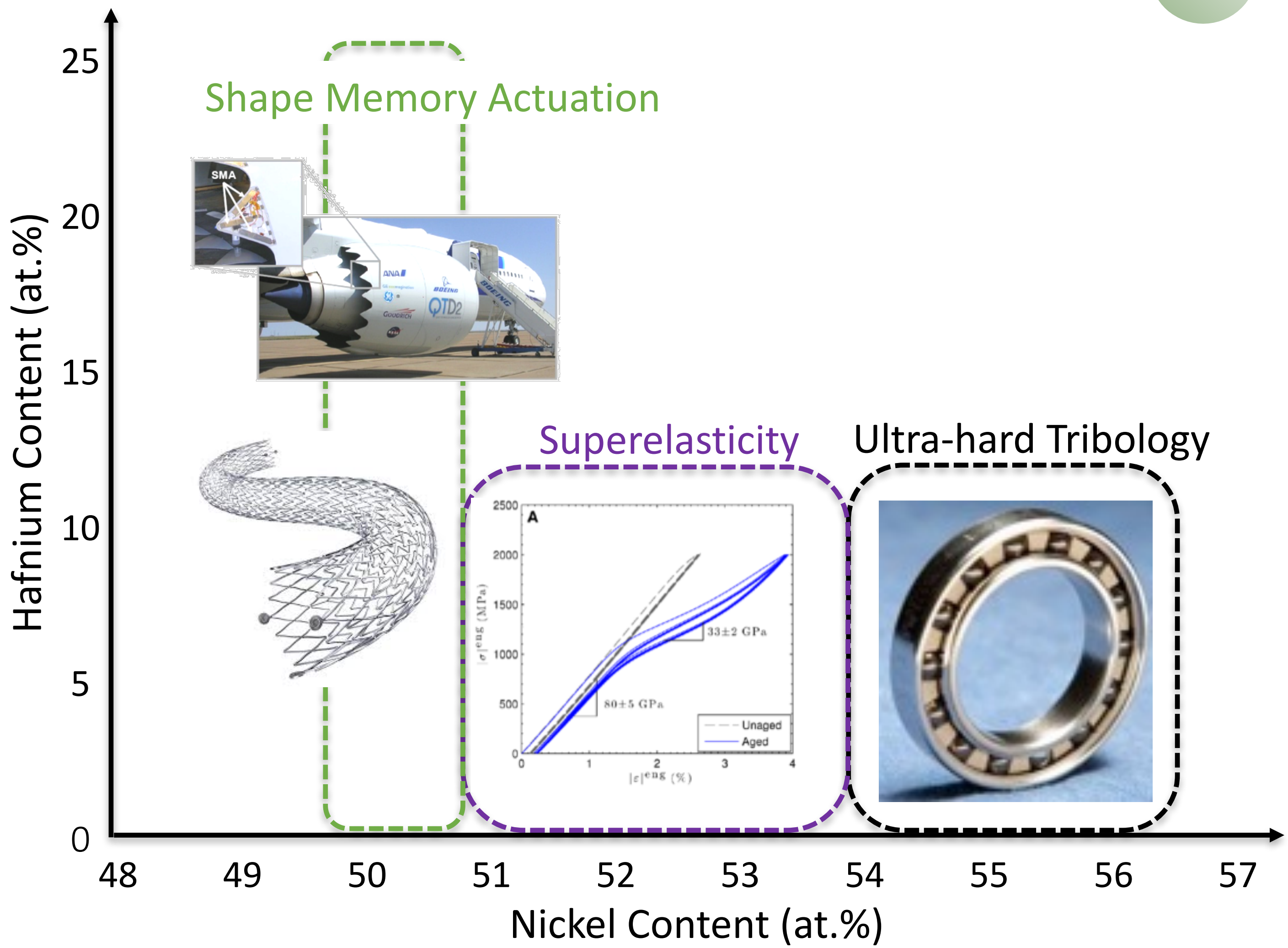
Adding Hf atoms in Ni-Ti:

- Lowers solvus temperature (1020ºC to 900ºC)
- Slows diffusion, optimum precipitation via air-cool
- High hardness (58 – 62 HRC) is retained

Residual stresses due to large undercooling can lead to fracture post-machining

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

Ni-Ti-Hf application space



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

Target design space of Ni-Ti-Hf

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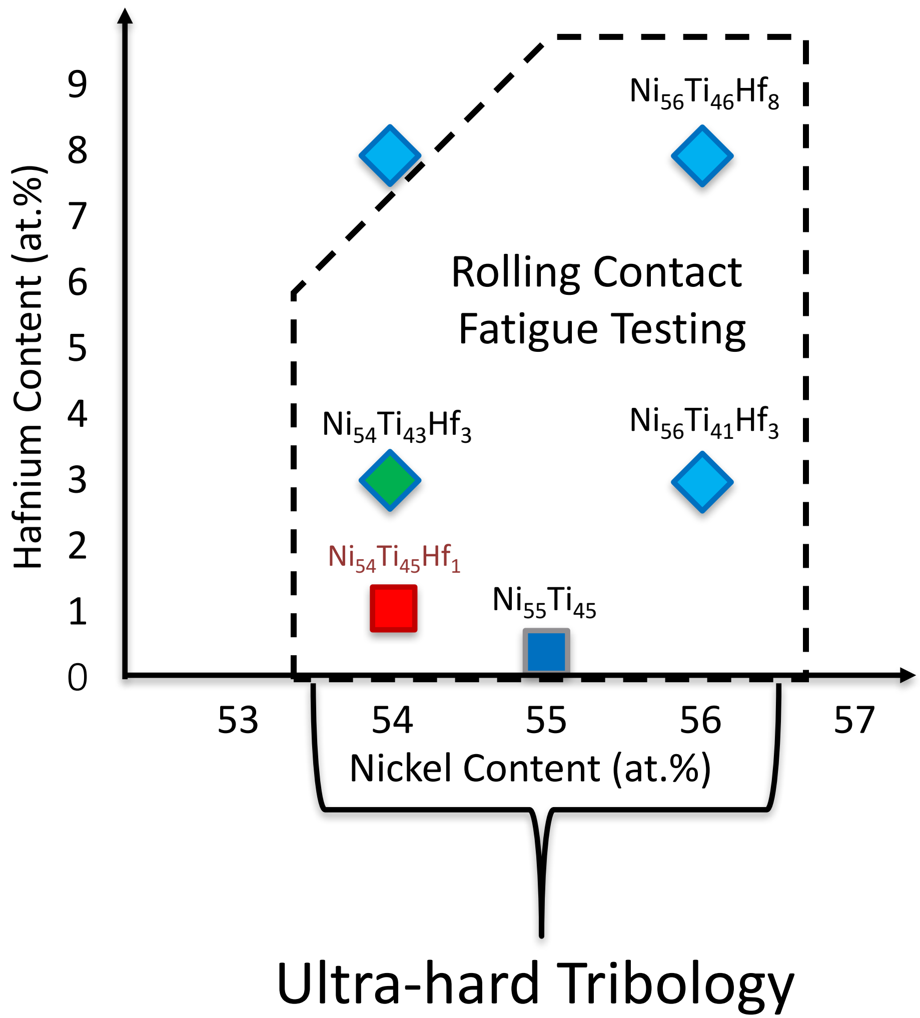
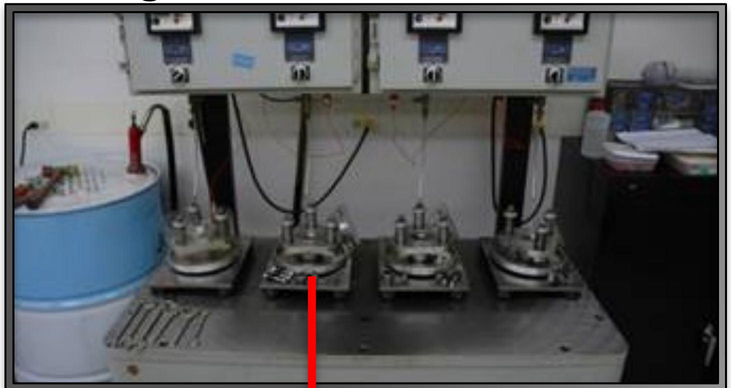
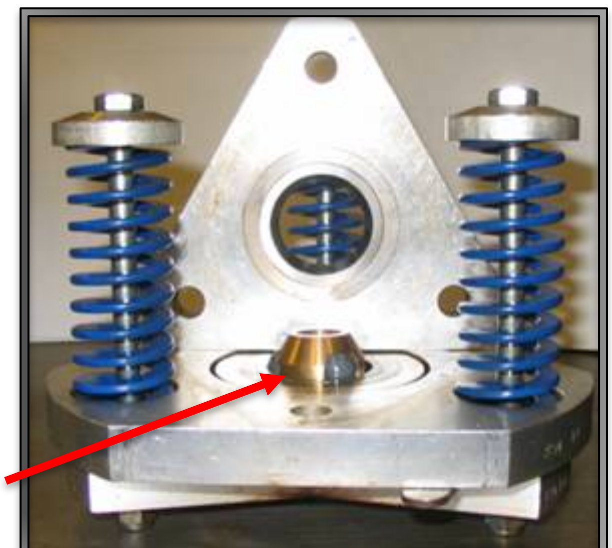


Rolling contact fatigue testing of Ni-Ti-Hf rods

Test rig

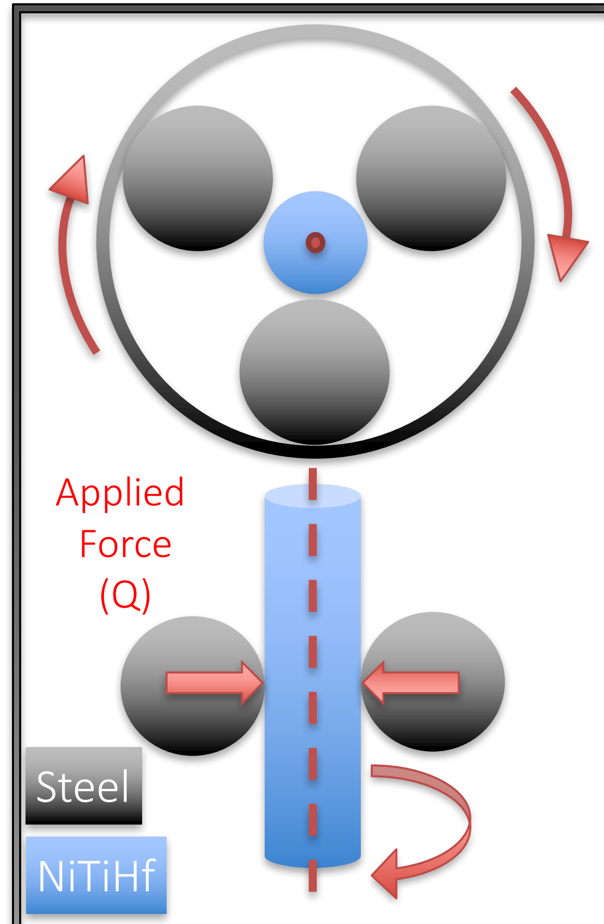


Spring loaded test head

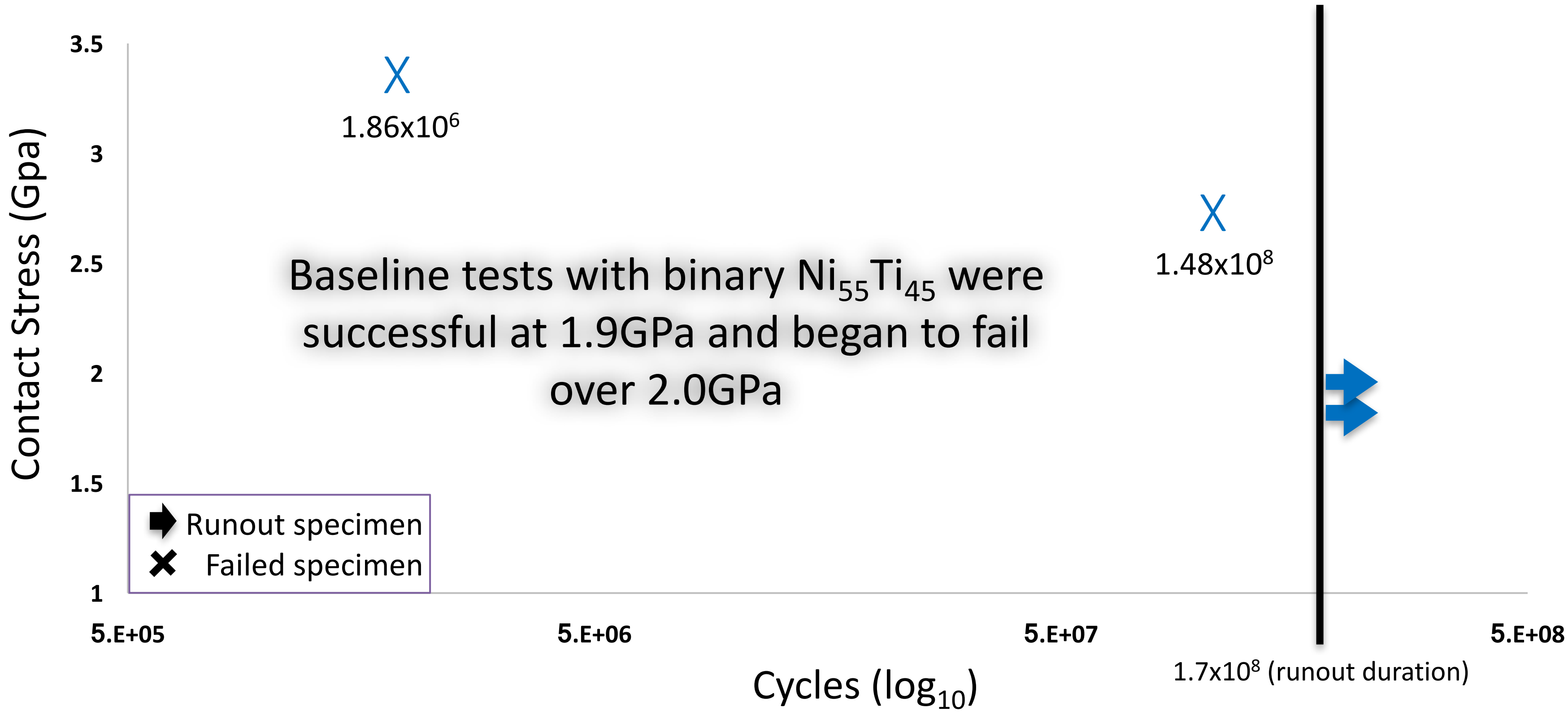


Ball bearing retainer

Three ball-on-rod RCF test configuration



RCF Tests: Composition and heat treatment → better performance



Previous Work

$Ni_{55}Ti_{45}$
$900C_{WQ}+400C(2hrs)_{AC}$

Dellacorte et al. Tribology Letters (2015)

RCF Tests: Composition and heat treatment ➔ better performance

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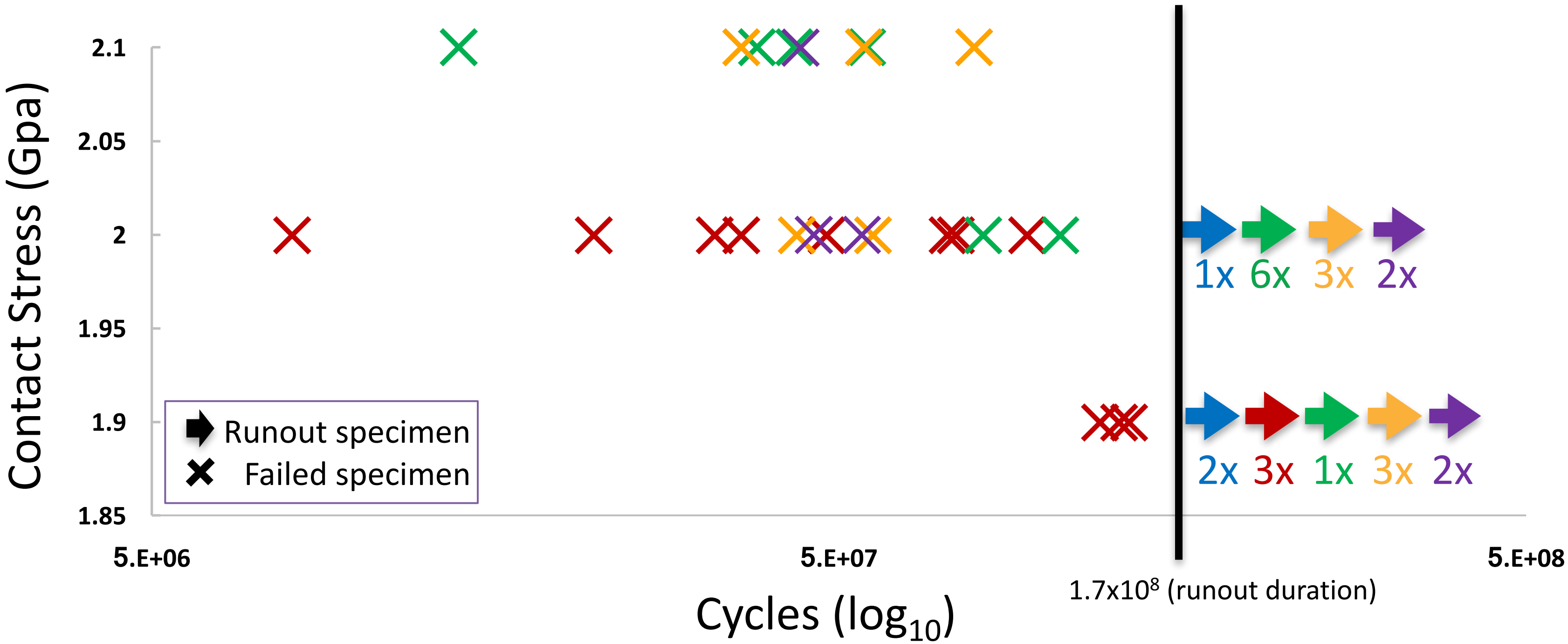

Previous Work

$Ni_{55}Ti_{45}$ $900C_{WQ}$ $+400C(2h)_{AC}$ 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

Current Work

$Ni_{56}Ti_{41}Hf_3$ $1050C_{WQ}+$ $300C(12h)_{AC}$ 752 HV	$Ni_{56}Ti_{36}Hf_8$ $1050C_{WQ}+$ $300C(12h)_{AC}$ $+550(4h)_{AC}$ 768 HV

RCF Tests: Composition and heat treatment
➔ better performance

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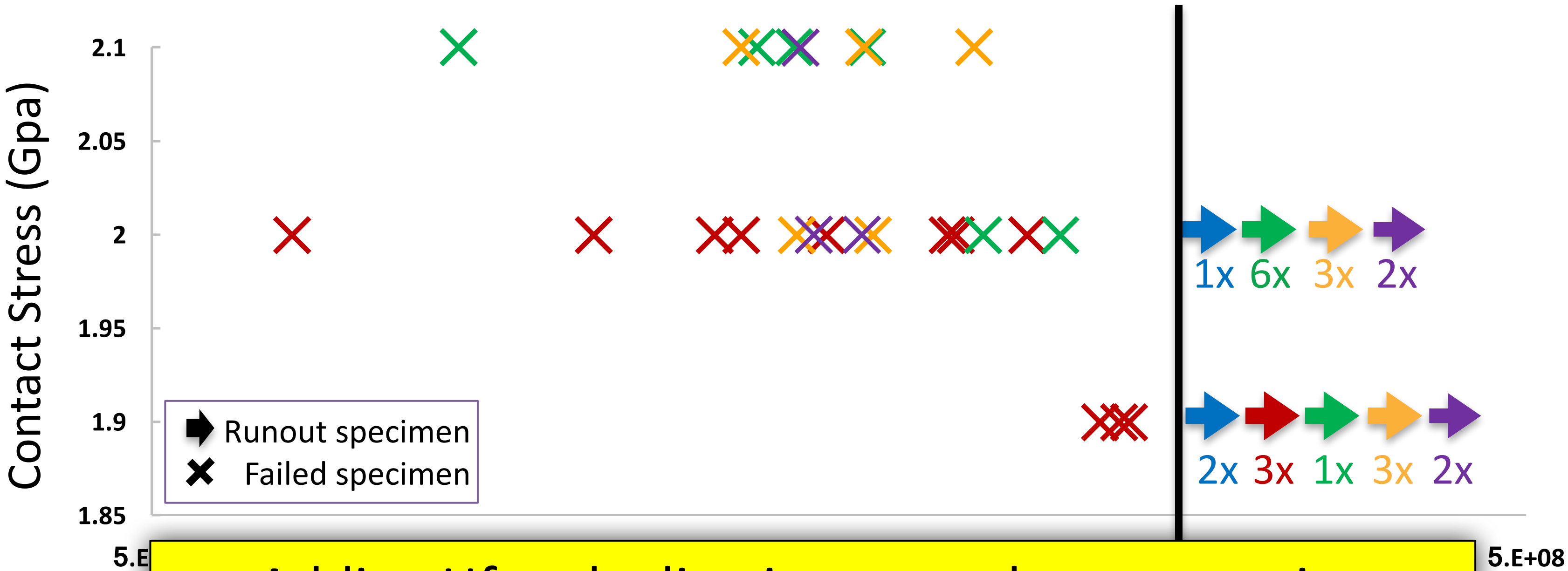

Adding Hf and adjusting secondary processing improves fatigue performance.
Hardness is important!

$Ni_{55}Ti_{45}$ 900C_{WQ} +400C(2h)$_{AC}$ 703 HV	1000C_{AC} +400C(2h)$_{AC}$ 677 HV	1050C_{WQ}+ 300C(12h)$_{AC}$ 724 HV	1050C_{WQ}+ 300C(12h)$_{AC}$ 752 HV	$Ti_{36}Hf_8$ 1050C_{WQ}+ 300C(12h)$_{AC}$ +550(4h)$_{AC}$ 768 HV

Target design space of Ni-Ti-Hf

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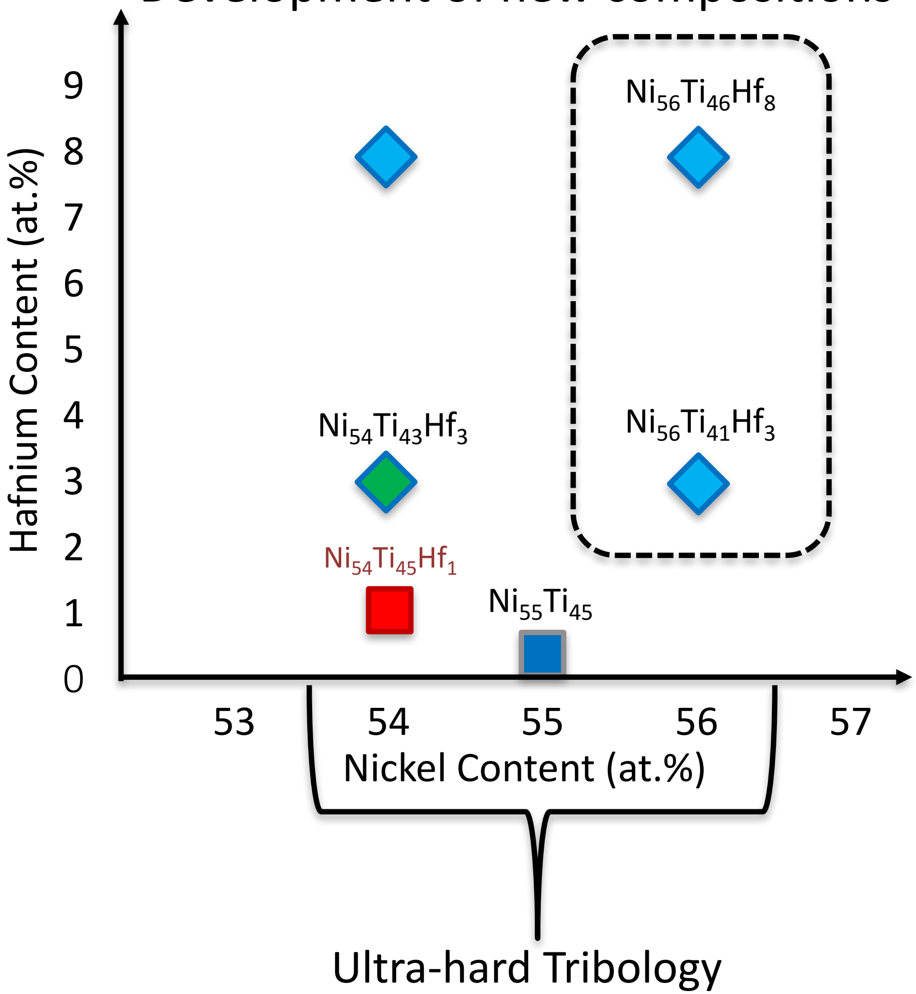
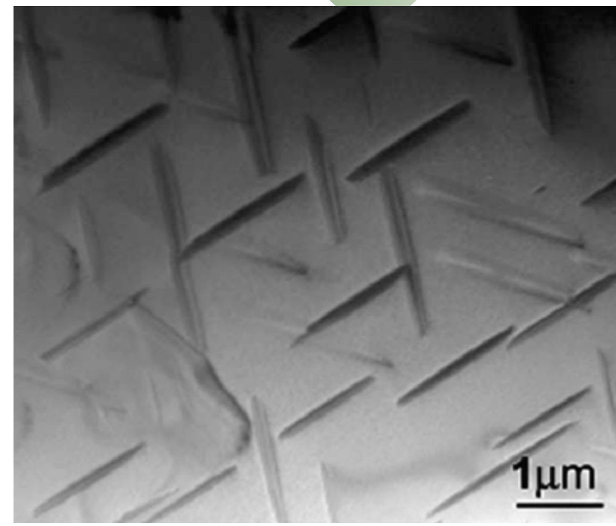
Development of new compositions

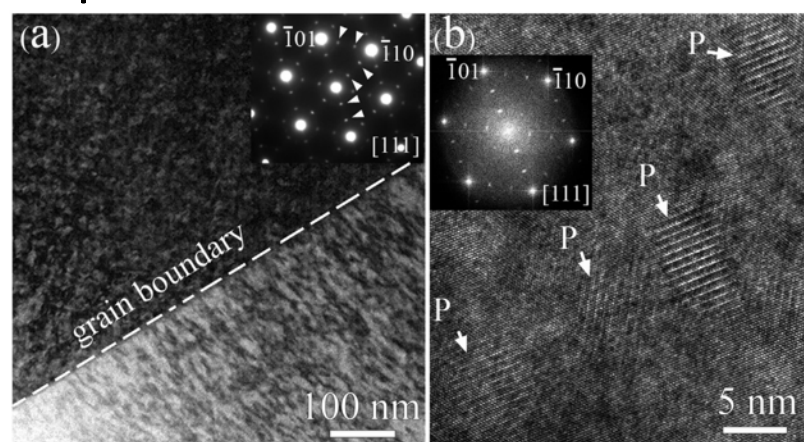


Ni_4Ti_3



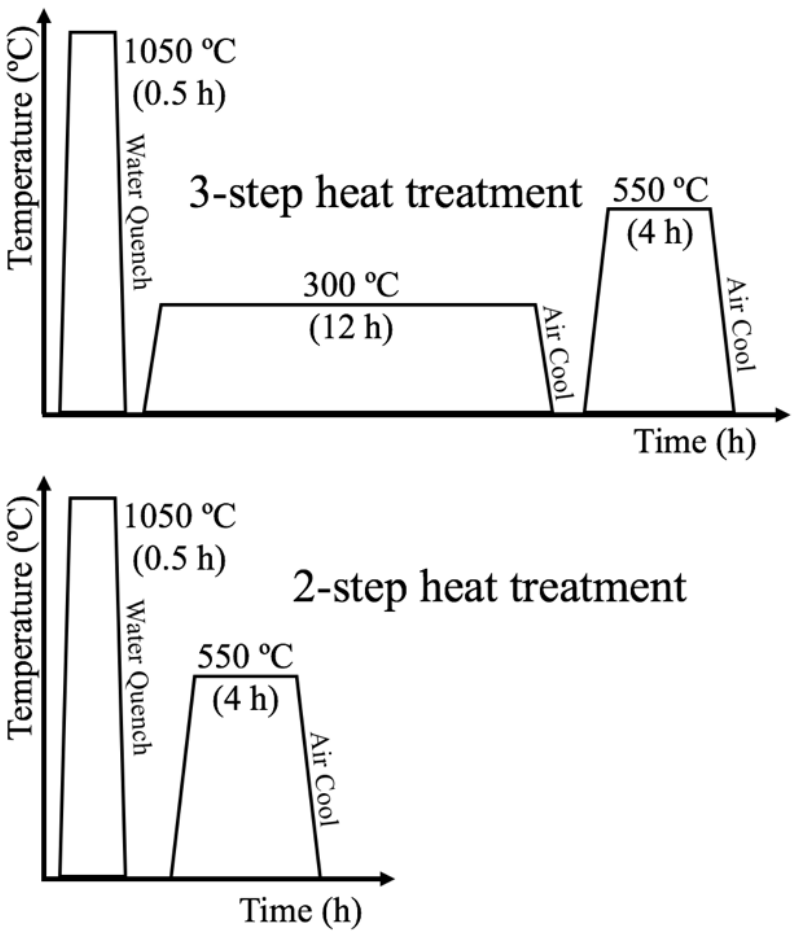
Yang et al. Scripta Mat. (2005)

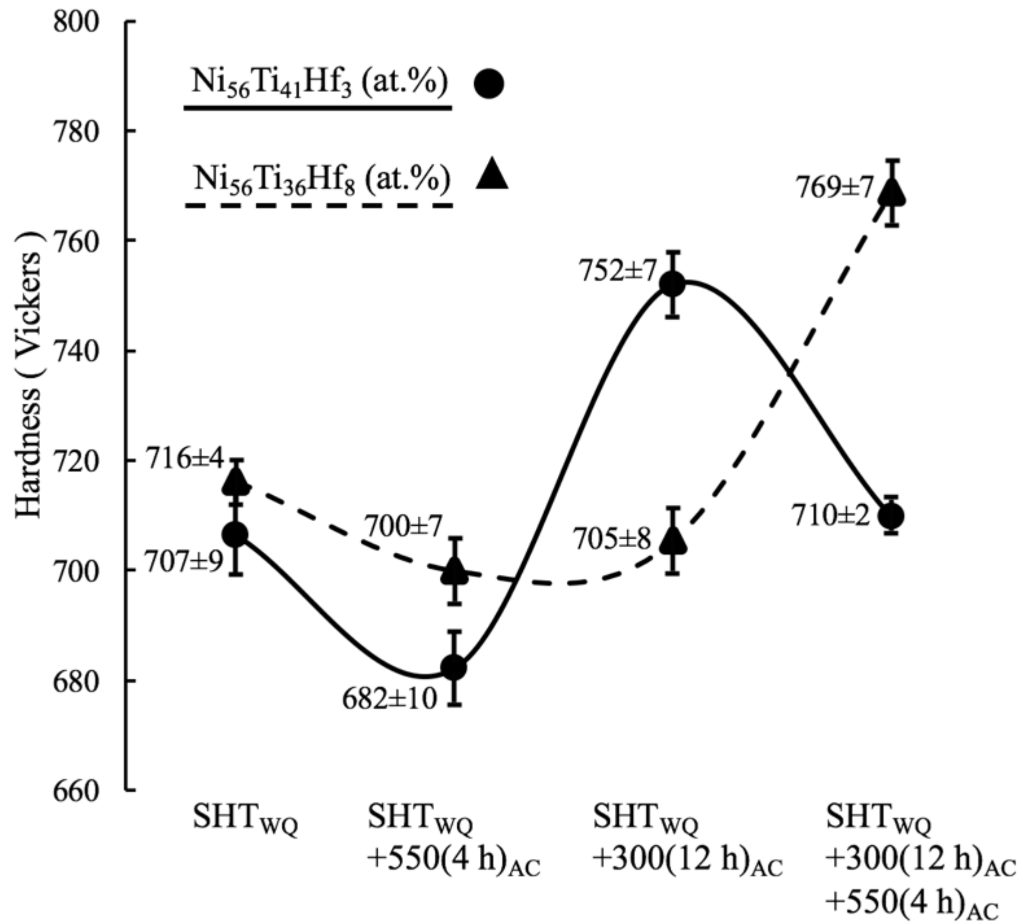
H-phase



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

Hardness evolution not consistent between compositions





➔ microstructure characterization necessary

$Ni_{56}Ti_{41}Hf_3$ → SHT_{WQ}

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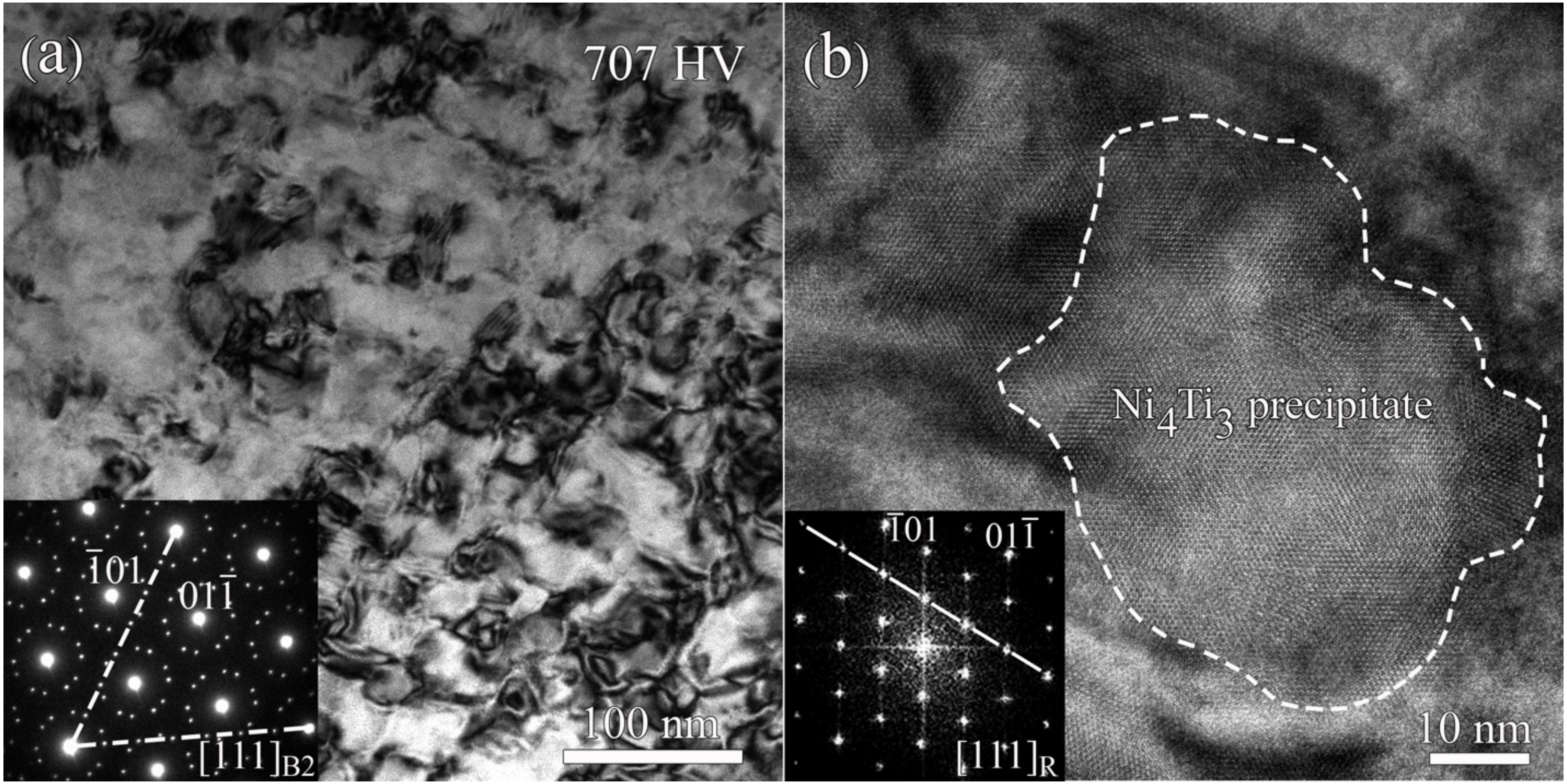

- → Blocky microstructure
- → No H-phase
- → High strain contrast between Ni_4Ti_3 and B2

Ni_4Ti_3 Size: 63 ± 16 nm
Ni_4Ti_3 Spacing: 42 ± 13 nm

$Ni_{56}Ti_{41}Hf_3$ → SHT_{WQ} + $550(4hrs)_{AC}$
Lowest hardness

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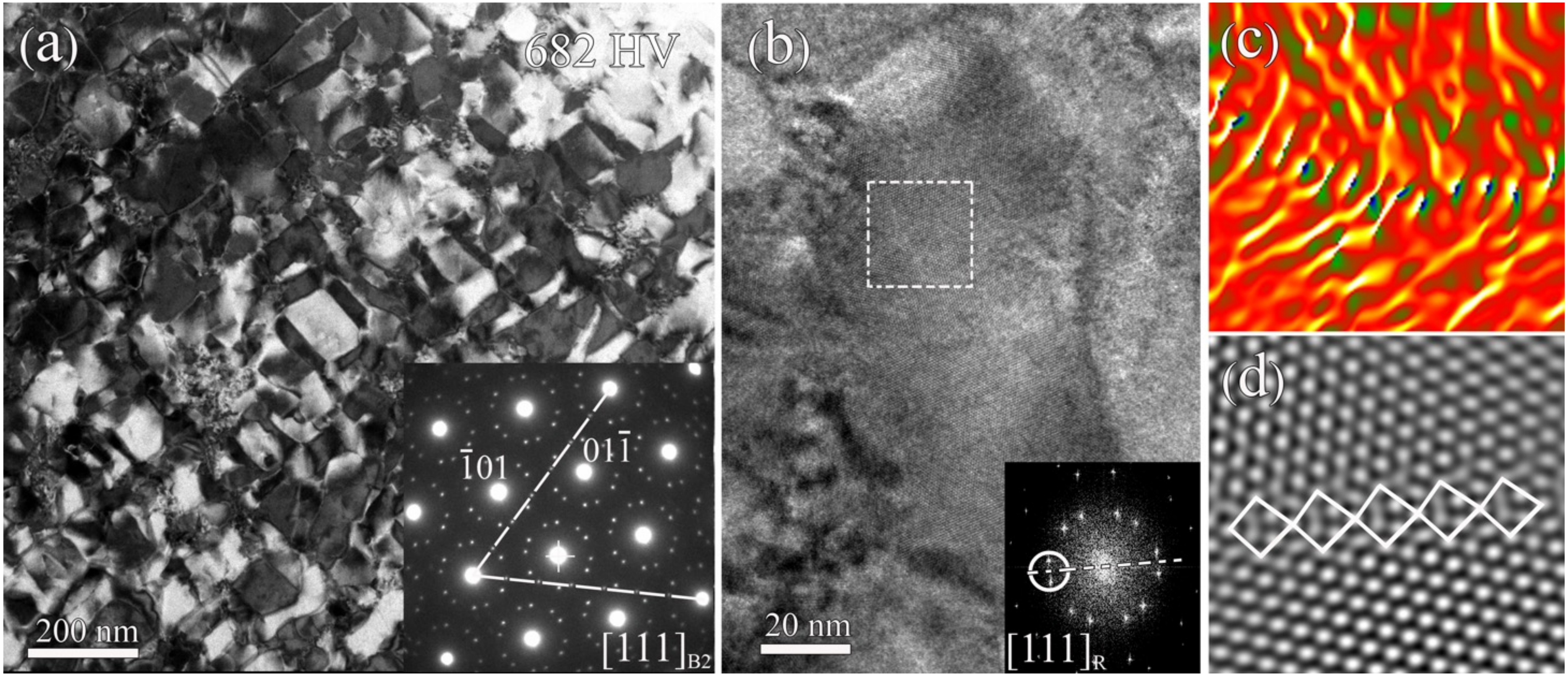

- ➔ Blocky microstructure
- ➔ No H-phase, coalesced Ni_4Ti_3
- ➔ Low strain contrast between Ni_4Ti_3 and B2

Ni_4Ti_3 Size: 113 ± 32 nm, 87 ± 19 nm
Ni_4Ti_3 Spacing: 92 ± 24 nm

$Ni_{56}Ti_{41}Hf_3$ → SHT_{WQ} + $300(12hrs)_{AC}$
Highest hardness

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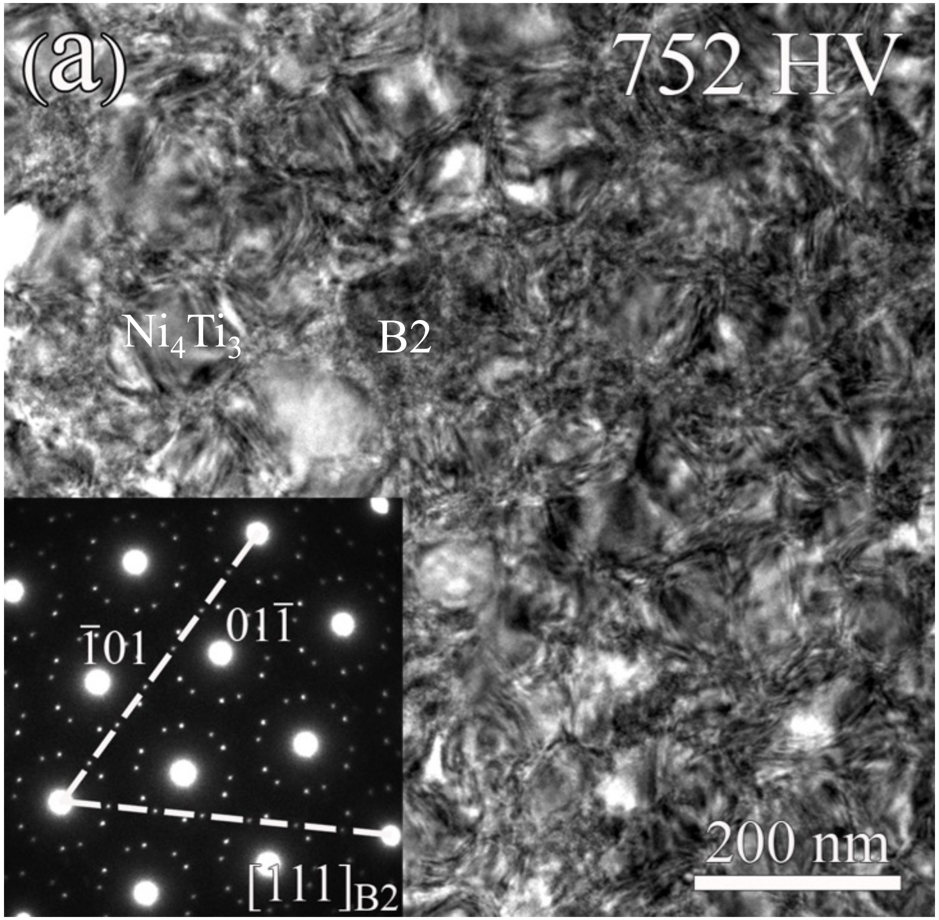

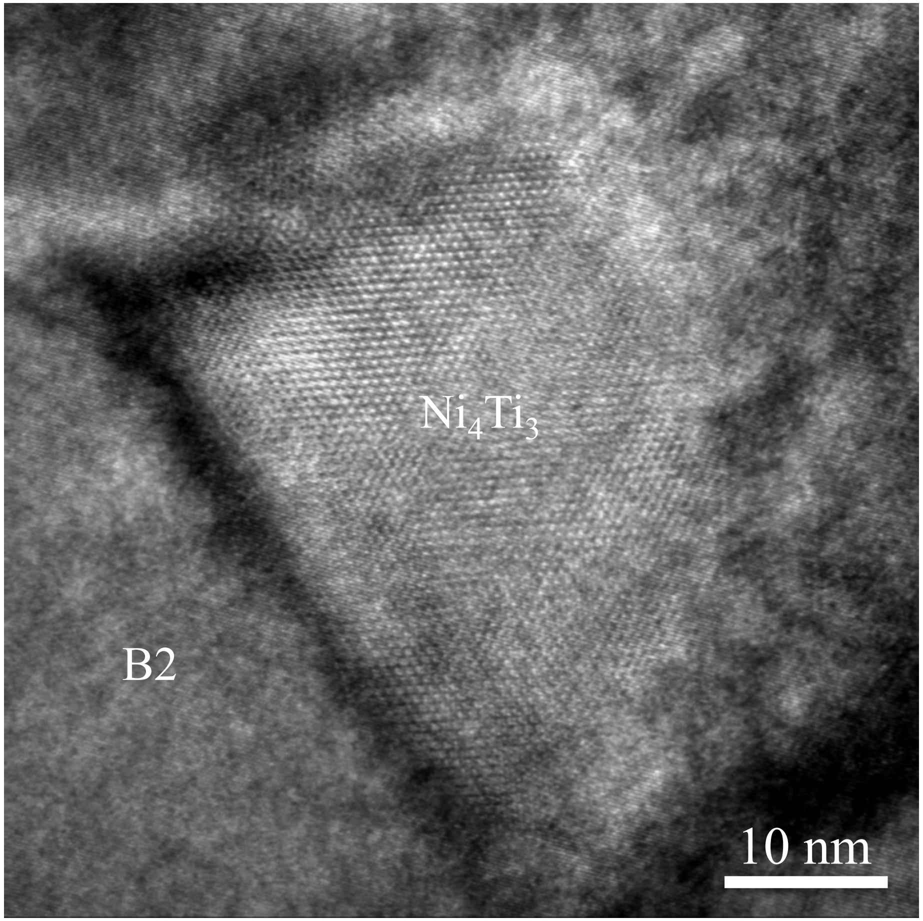

- ➔ Blocky microstructure
- ➔ No H-phase
- ➔ High strain contrast between Ni_4Ti_3 and B2

Ni_4Ti_3 Size: 65 ± 21 nm

Ni_4Ti_3 Spacing: 51 ± 19 nm

$Ni_{56}Ti_{41}Hf_3$ ➔ SHT_{WQ} + $300(12hrs)_{AC}$
Highest hardness

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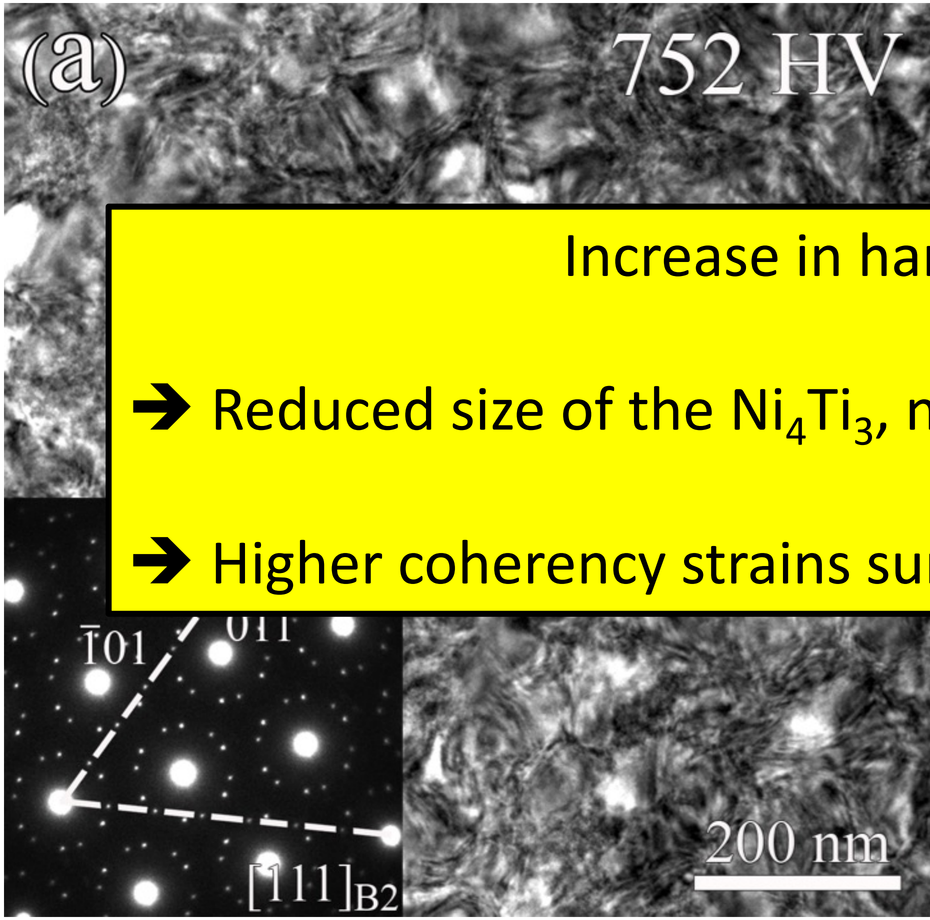

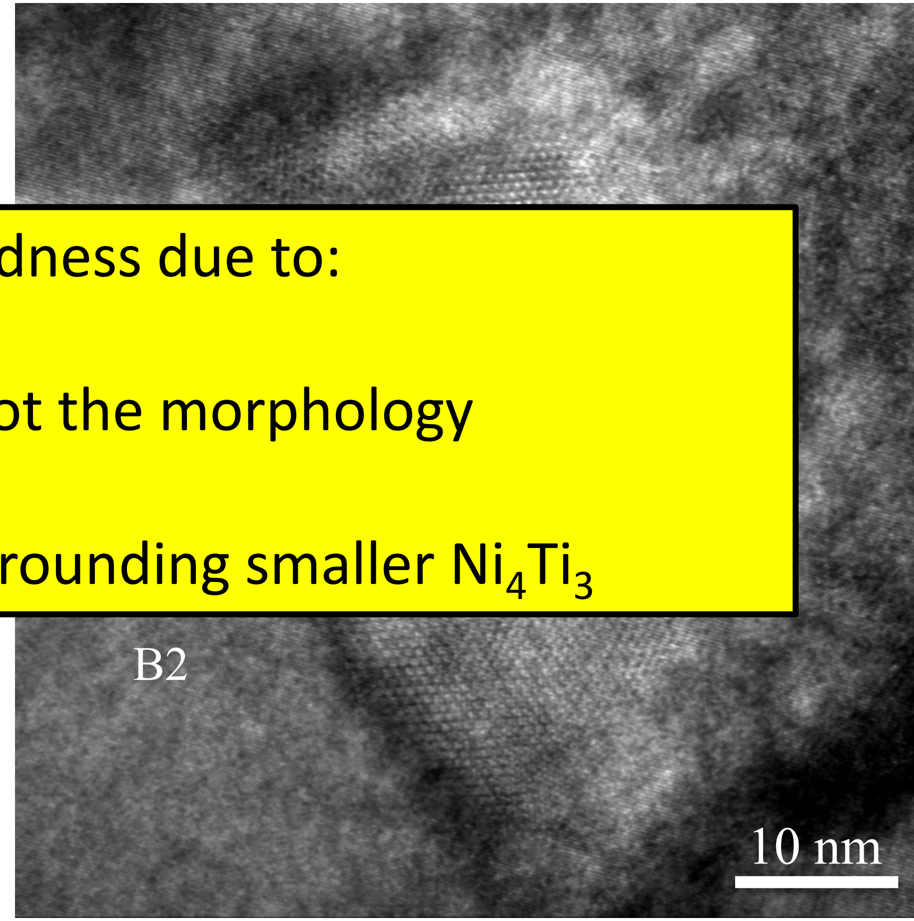

Increase in hardness due to:

➔ Reduced size of the Ni_4Ti_3, not the morphology

➔ Higher coherency strains surrounding smaller Ni_4Ti_3

➔ Blocky microstructure
➔ No H-phase
➔ High strain contrast between Ni_4Ti_3 and B2

Ni_4Ti_3 Size: 65 ± 21 nm
Ni_4Ti_3 Spacing: 51 ± 19 nm

$Ni_{56}Ti_{36}Hf_{8}$ → SHT_{WQ}

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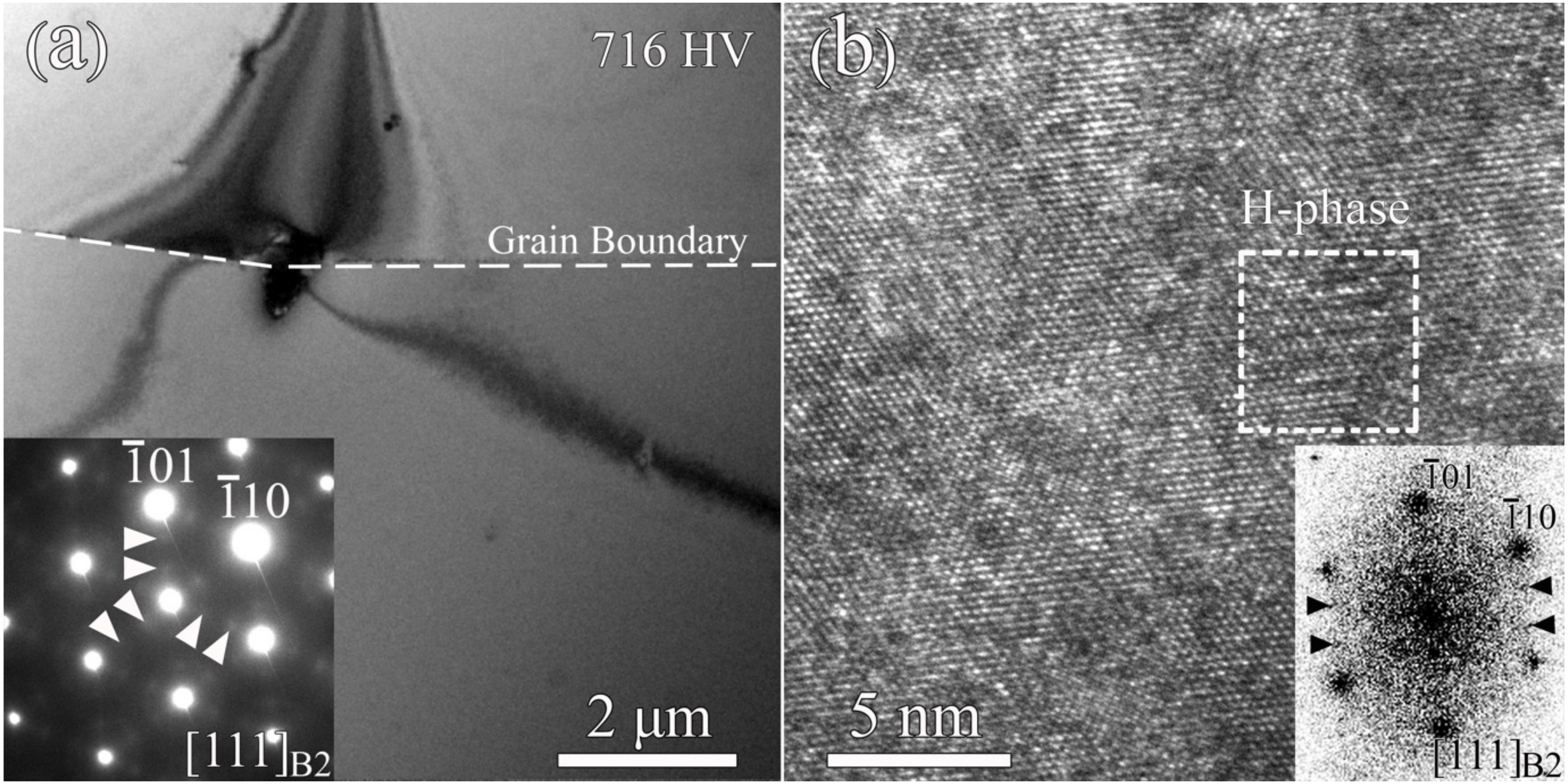

- → No visible secondary precipitation from low-magnification
- → Rare nano-sized H-phase (<5nm) in B2 matrix
- → Indication of elemental clustering prior to H-phase nucleation

$Ni_{56}Ti_{36}Hf_8$ ➔ SHT_{WQ} + $550(4hrs)_{AC}$
Lowest hardness

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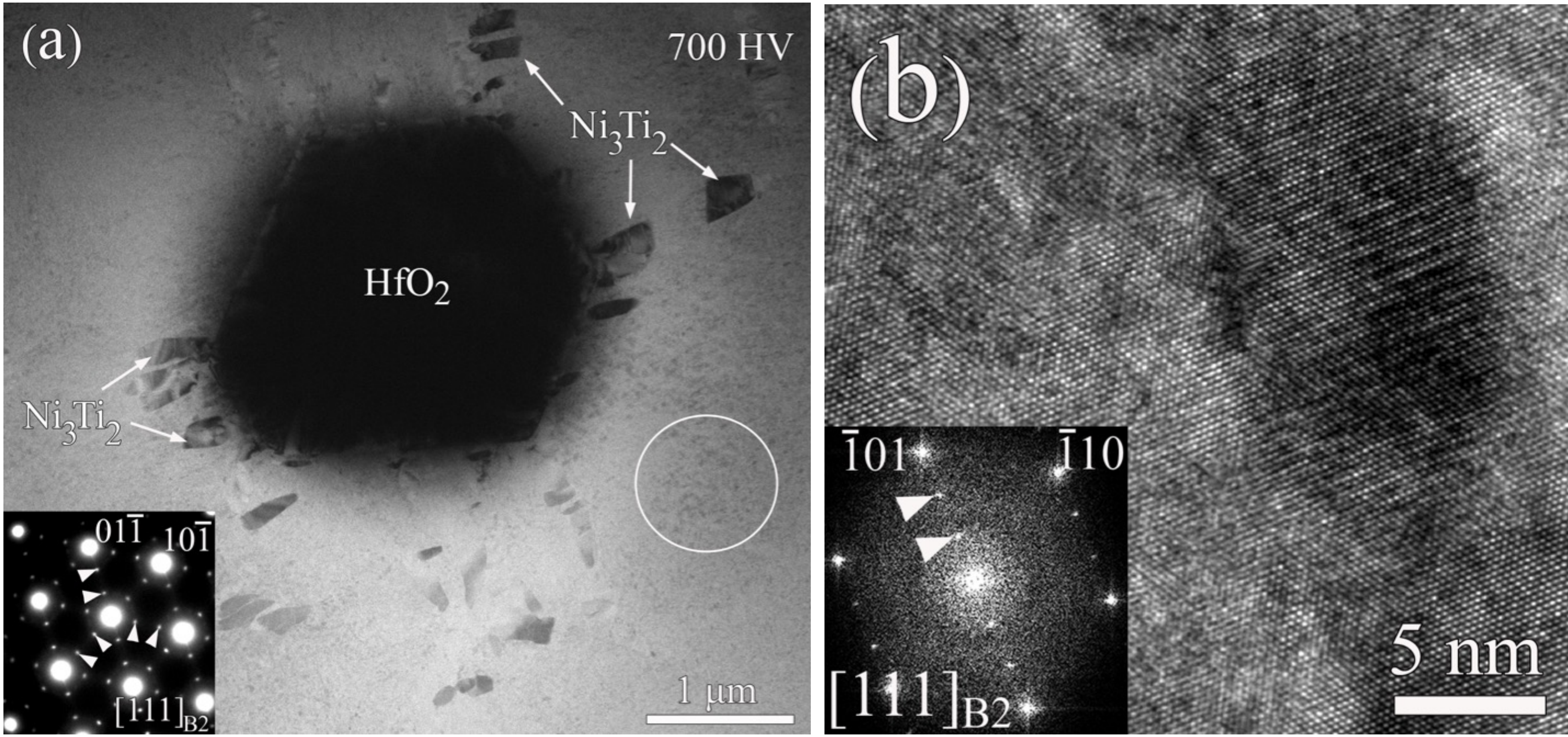

- ➔ No blocky microstructure
- ➔ Dense nano H-phase in B2 matrix
- ➔ No Ni_4Ti_3 or Ni_3Ti_2 precipitates in matrix
- ➔ Large heterogeneous islands (0.3-0.5 μm)

H-phase Size: 21 ± 6 nm, 8 ± 2 nm

H-phase Spacing: 17 ± 6 nm

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

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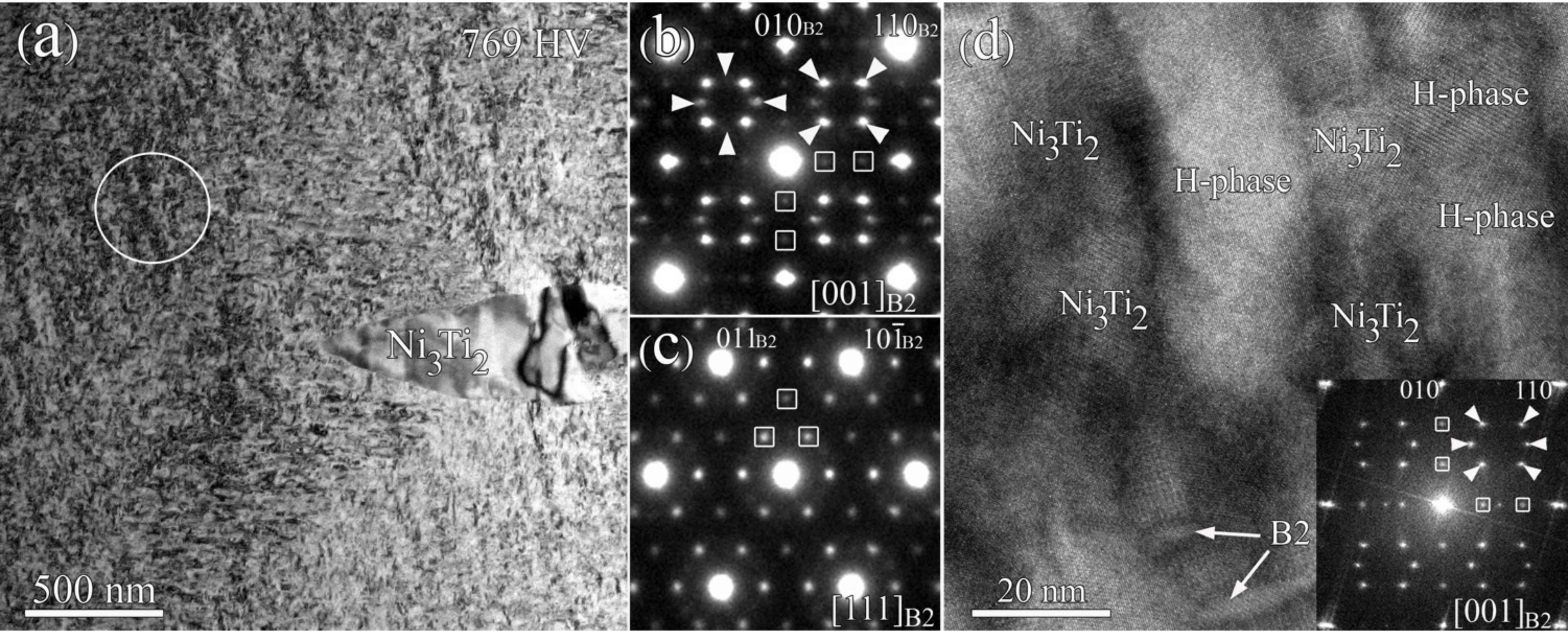

- ➔ No blocky microstructure
- ➔ Dense nano-Ni_3Ti_2 and nano-H-phase in B2 matrix
- ➔ Large heterogeneous islands (0.4-0.6 μm)

H-phase Size: 23 ± 5 nm, 12 ± 3 nm
H-phase Spacing: 7 ± 2nm

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

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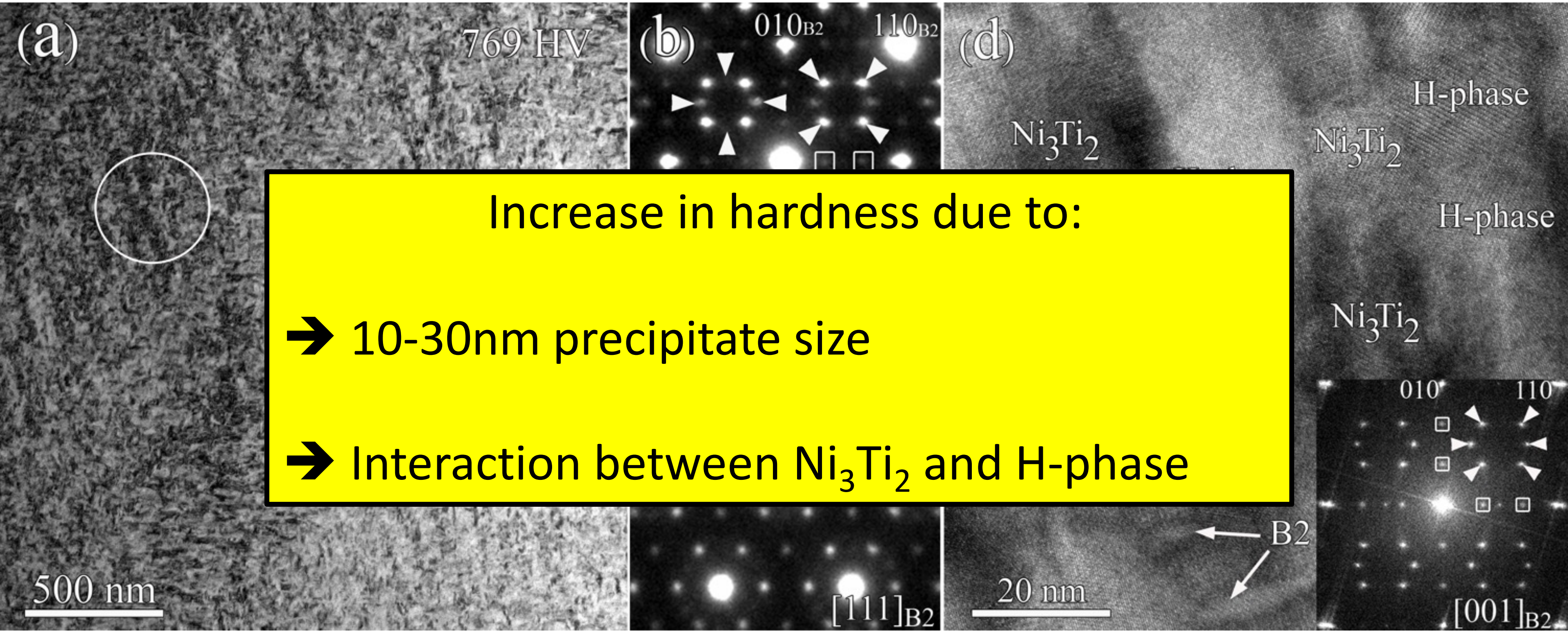

Increase in hardness due to:

→ 10-30nm precipitate size

→ Interaction between Ni_3Ti_2 and H-phase

→ No blocky microstructure

→ Dense nano-Ni_3Ti_2 and nano-H-phase in B2 matrix

→ Large heterogeneous islands (0.4-0.6 μm)

H-phase Size: 23 ± 5 nm, 12 ± 3 nm
H-phase Spacing: 7 ± 2nm

Conclusions for Ni-Ti-Hf

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- ➔ Blocky Ni_4Ti_3 is dominant strengthening phase in $Ni_{56}Ti_{41}Hf_3$.

- ➔ Nano-scale H-phase is dominant strengthening phase in $Ni_{56}Ti_{36}Hf_8$. Very different mechanism that produces similar hardness values to $Ni_{56}Ti_{41}Hf_3$.

- ➔ Increasing Hf content hinders Ni_4Ti_3 formation and allows for tailored heat treatment schedule.

- ➔ Multiple routes can be taken to obtain optimum hardness levels. Microstructure is completely different, but similar properties are obtained.

- ➔ Tribology and compression testing on varied 56at.% Ni compositions show failure at 2.0 – 2.1 GPa.

Gantt chart

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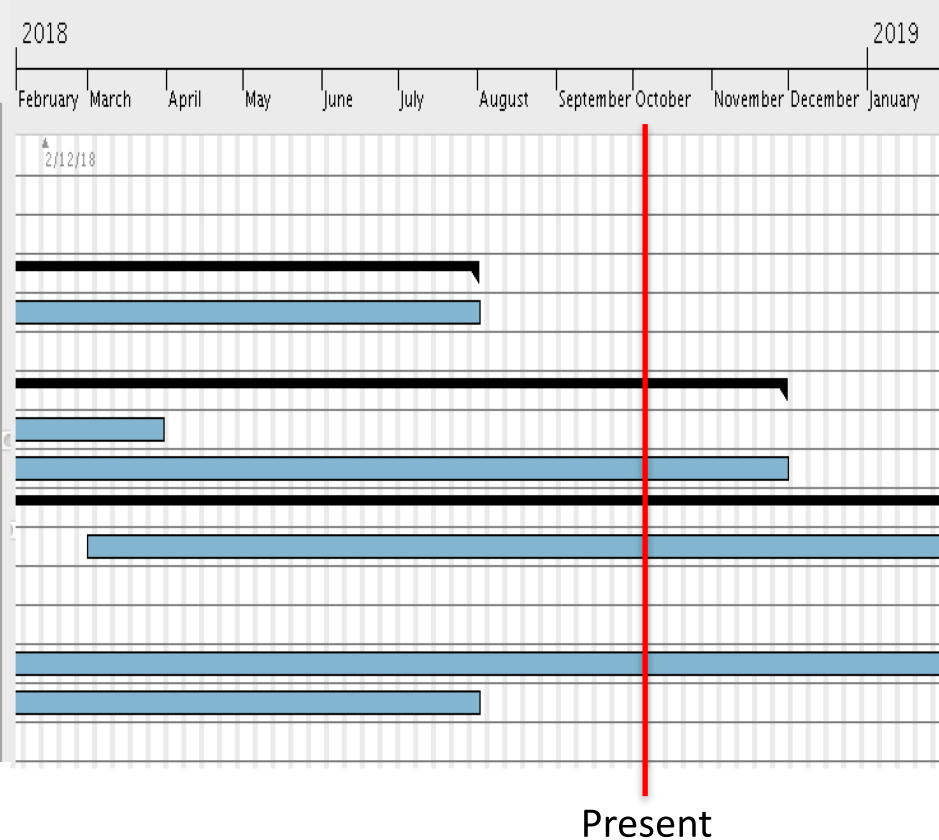
ame	Begin da...	End da...
Residual stress and hardness testing on NiTi & NiTiHf1	8/3/15	8/1/16
XRD analysis of residual microstresses	8/3/15	1/1/16
Heat treatments & hardness testing for NiTiHf1	12/1/15	8/1/16
Rolling contact fatigue characterization of NiTiHf1	11/2/15	2/1/18
Failure analysis (XRD, OM, TEM, SEM)	6/1/16	2/1/18
RCF testing	11/2/15	11/2/...
Time/Temperature/Transformation of NiTiHf1	2/1/17	6/1/18
Ex-situ elucidation of T-T-T space (coarse resolution)	2/1/17	5/1/18
In-situ TEM & XRD studies of transformation kinetics & therm...	4/3/17	6/1/18
Alloy optimization - vary nickel and hafnium contents by 1-8 at%	1/1/16	9/30/...
In-situ studies of transformation kinetics & thermodynamics	6/1/18	8/1/19
Screen hardness, strengths, and residual stresses of alloy ma...	1/1/16	12/1/...
Ex-situ T-T-T mapping of most promising/interesting alloys	6/1/16	8/1/17
RCF testing of most promising/interesting alloys	11/1/17	9/30/...
Failure analysis	6/1/17	8/1/18



Thank you very much!

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Acknowledgements:

Behnam Aminahmadi (Mines)

Robert Williams (CEMAS)

Othmane Benafan (NASA GRC)

Christopher Dellacorte (NASA GRC)

Ronald Noebe (NASA GRC)

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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

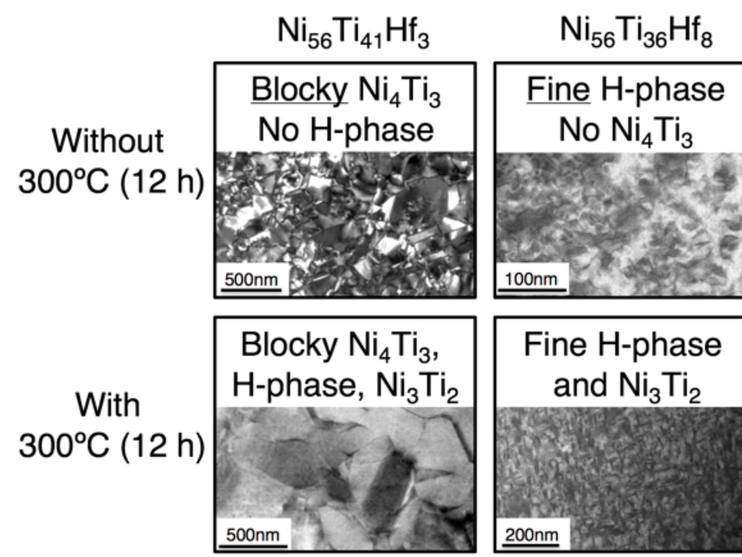
- Novel Ni-rich alloys provide ultra-hard optimized microstructures designed for space-age tribology applications.

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

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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