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Center for Advanced Non-Ferrous Structural Alloys

An Industry/University Cooperative Research Center

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

Fall 2019 Semi-Annual Meeting

Colorado School of Mines, Golden, CO

October 9 - 11, 2019

Student: Sean Mills (Mines)

Faculty: Aaron Stebner (Mines), Behnam Aminahmadi (Mines)

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

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

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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 $Ni_{56}Ti_{36}Hf_8$, $Ni_{54}Ti_{45}Hf_1$ and $Ni_{55}Ti_{45}$ alloys
- Identification and structure analysis of $Ni_{16}Ti_{11}$ phase
- Thesis writing

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. Subsurface deformation analysis of $Ni_{56}Ti_{36}Hf_8$ alloy	80%	●
5. Alloy optimization – vary nickel and hafnium contents by 1-8 at%	90%	●

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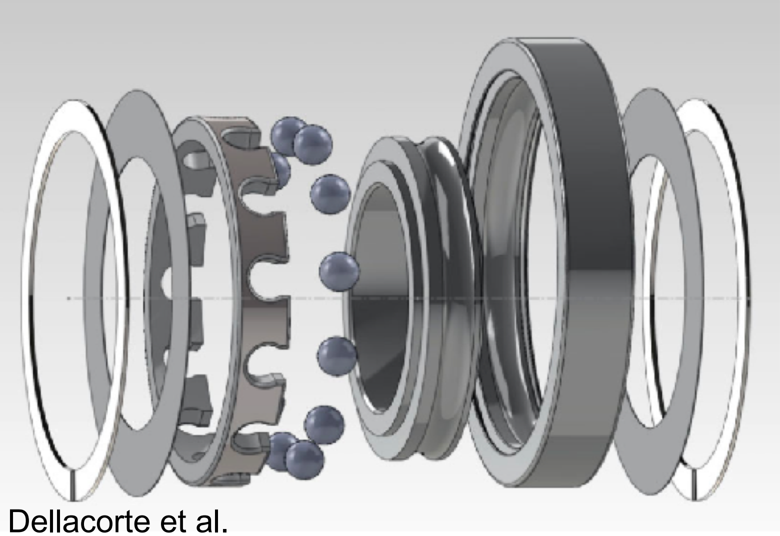
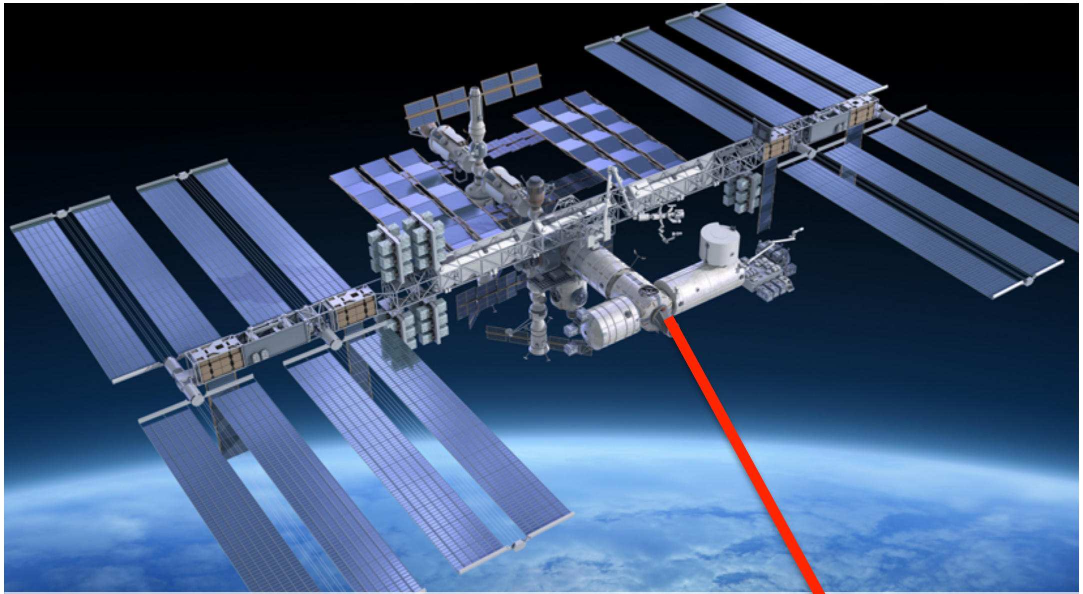
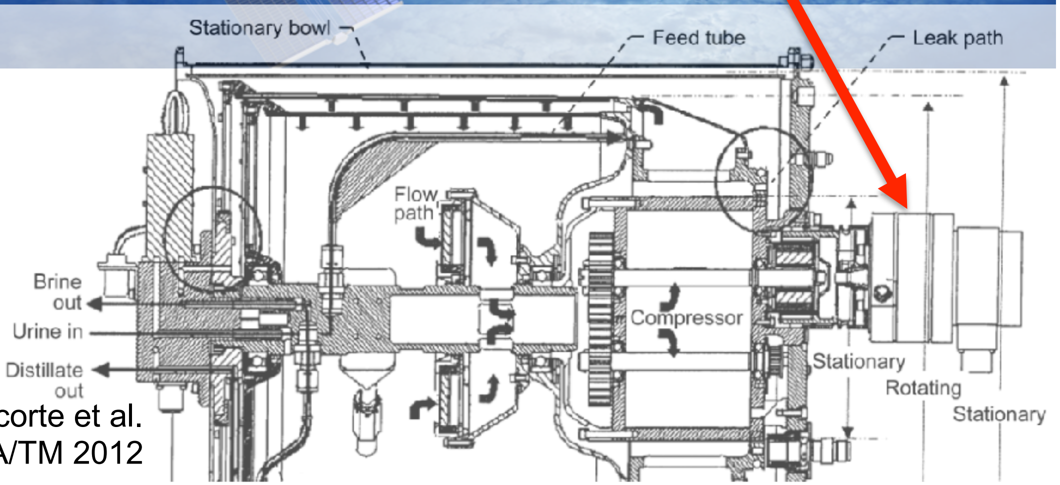
Application: Water recycling system on International Space Station

Rotating Centrifuge Bearing



Dellacorte et al.
NASA/TM 2012





Dellacorte et al.
NASA/TM 2012

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

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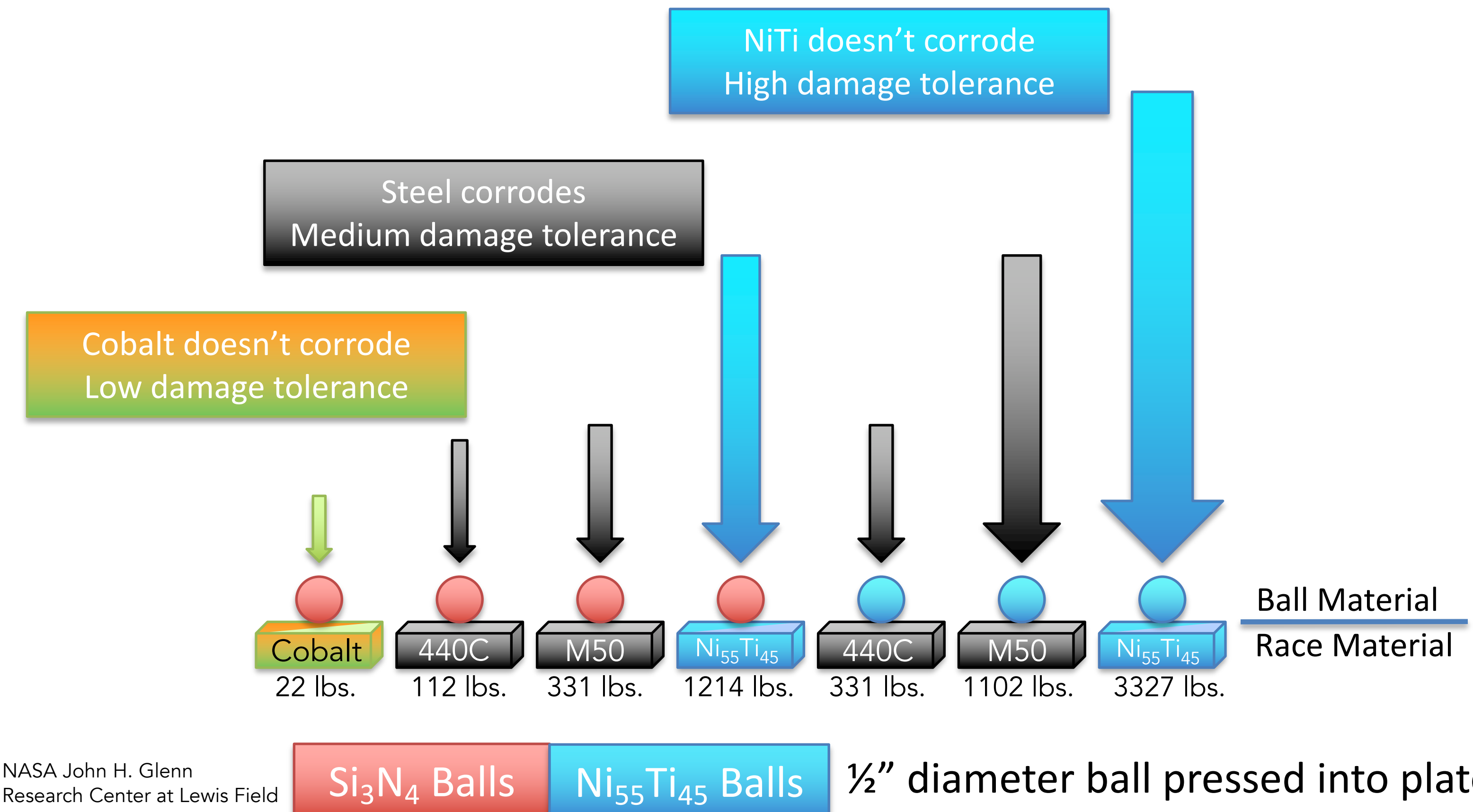
Nickel-rich Ni-Ti alloys show superior damage resistance

Dent Resistance Load Capacity



½" diameter ball pressed into plate

NASA John H. Glenn Research Center at Lewis Field

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

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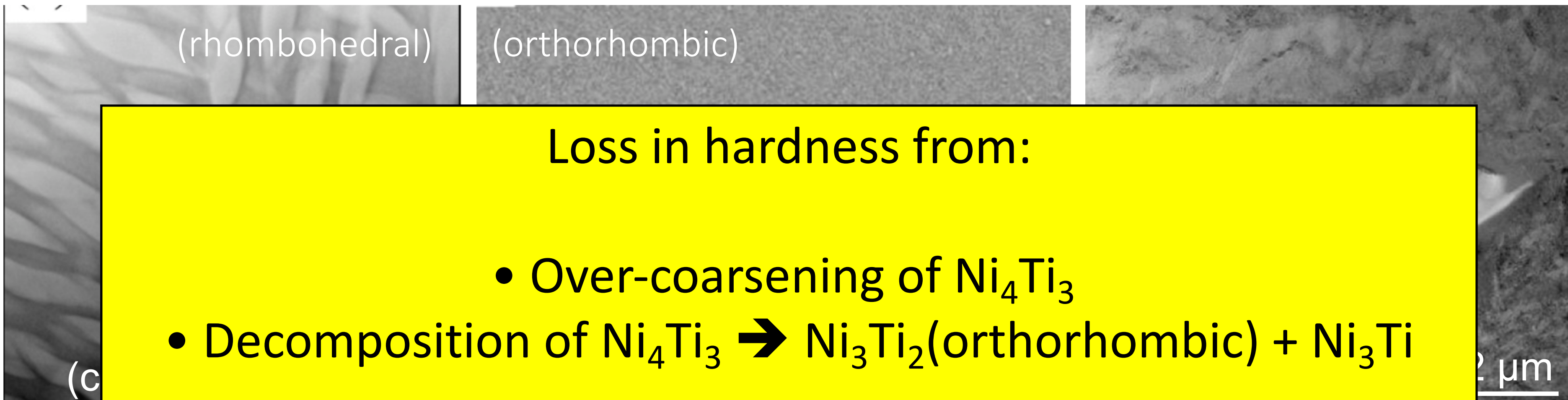
$B2_0$ ➔ $B2_1 + Ni_4Ti_3$ ➔ $B2_2 + Ni_3Ti_2$ ➔ $B2_3 + Ni_3Ti$

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



17

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…

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

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Binary Ni-Ti bearing races are susceptible to untimely failures

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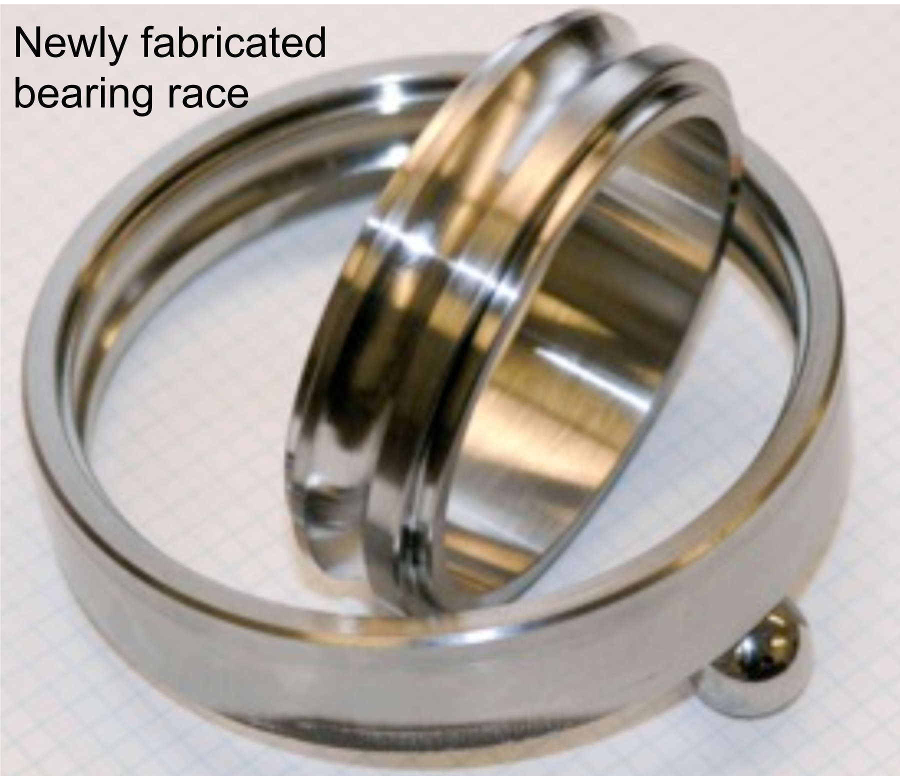

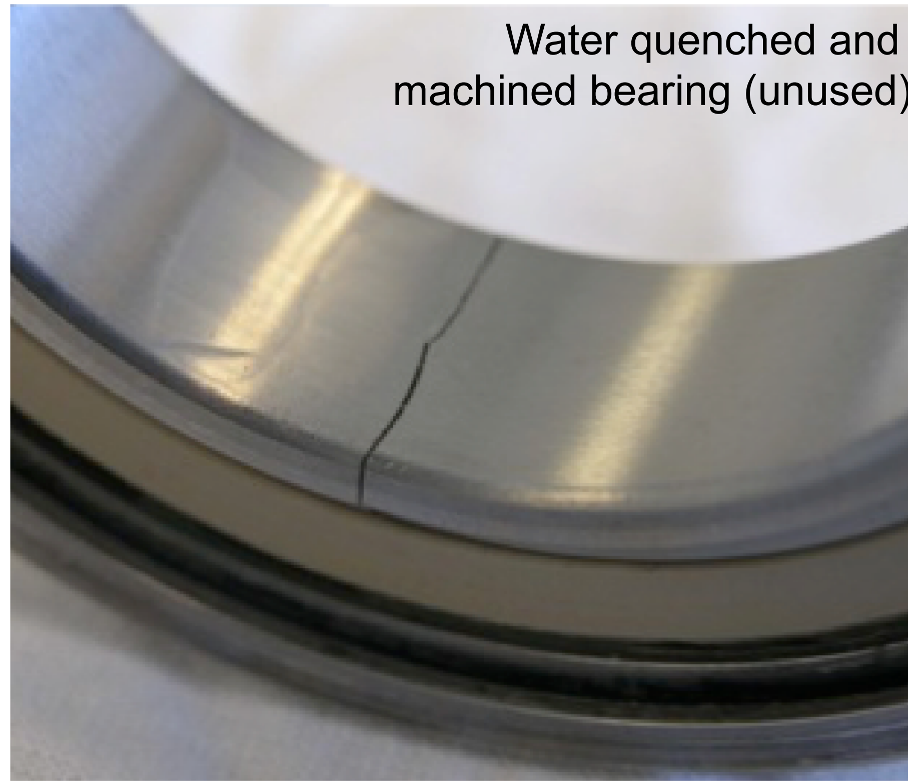

National Aeronautics a
John H. Glenn Resea

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

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Subtle Hf additions in Ni-Ti

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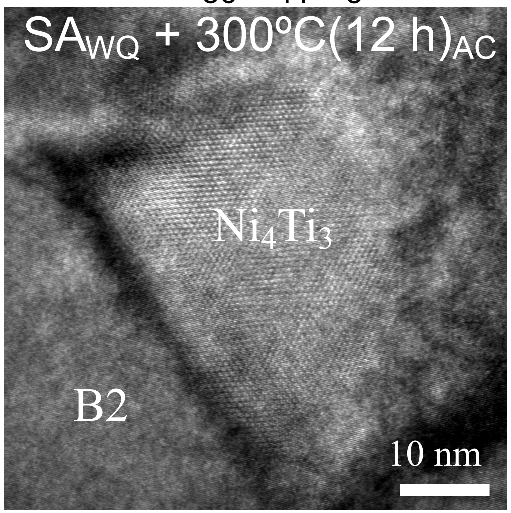
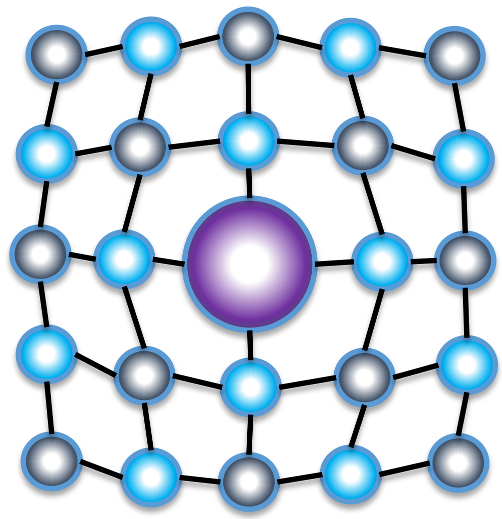
$Ni_{56}Ti_{41}H_3$

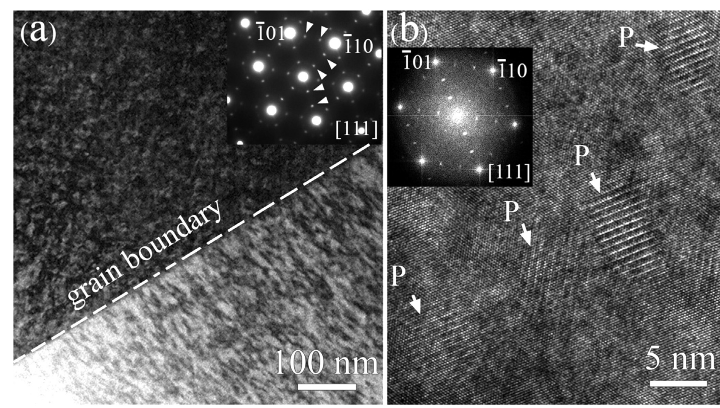


← Slows Ni_4Ti_3 kinetics (NiTiHf retains high hardness with air cooling)



← Hf solid-solution strengthening

H-phase precipitation strengthening →



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

Bearing grade hardness (58 – 62 HRC) is retained

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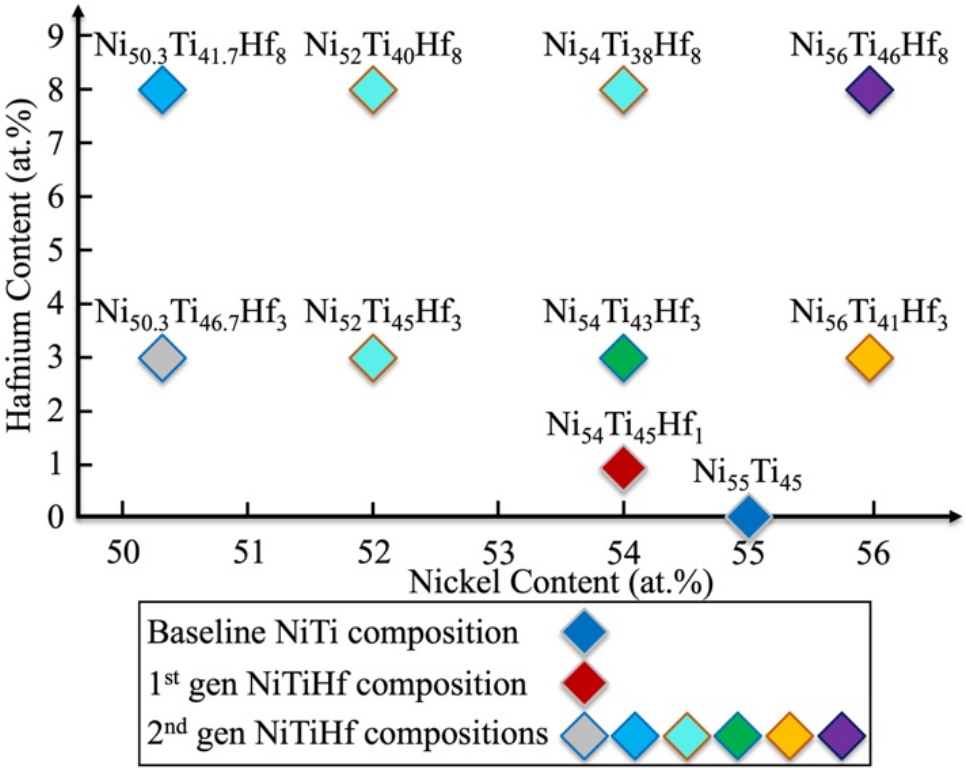
NiTiHf Alloy Optimization



Composition (at. %)	Heat treatment	Hardness (HV)
$Ni_{56}Ti_{36}Hf_8$	SA_{WQ} + 300ºC (12 h) + 550ºC (4 h)	769
$Ni_{54}Ti_{38}Hf_8$	SA_{WQ} + 300ºC (12 h) + 550ºC (4 h)	742
$Ni_{52}Ti_{40}Hf_8$	SA_{WQ} + 300ºC (12 h) + 400ºC (4 h)	712
$Ni_{50.3}Ti_{41.7}Hf_8$	SA_{WQ} + 300ºC (12 h) + 400ºC (4 h)	639
$Ni_{56}Ti_{41}Hf_3$	SA_{WQ} + 300ºC (12 h)	752
$Ni_{54}Ti_{43}Hf_3$	SA_{WQ} + 300ºC (12 h)	735
$Ni_{52}Ti_{45}Hf_3$	SA_{WQ} + 300ºC (12 h) + 400ºC (1.5 h)	705
$Ni_{50.3}Ti_{46.7}Hf_3$	SA_{WQ} + 300ºC (12 h) + 400ºC (1.5 h)	692
$Ni_{54}Ti_{45}Hf_1$	SA_{WQ} + 400ºC (.5 h)	677
$Ni_{55}Ti_{45}$	SA_{WQ} + 400ºC (1 h)	688

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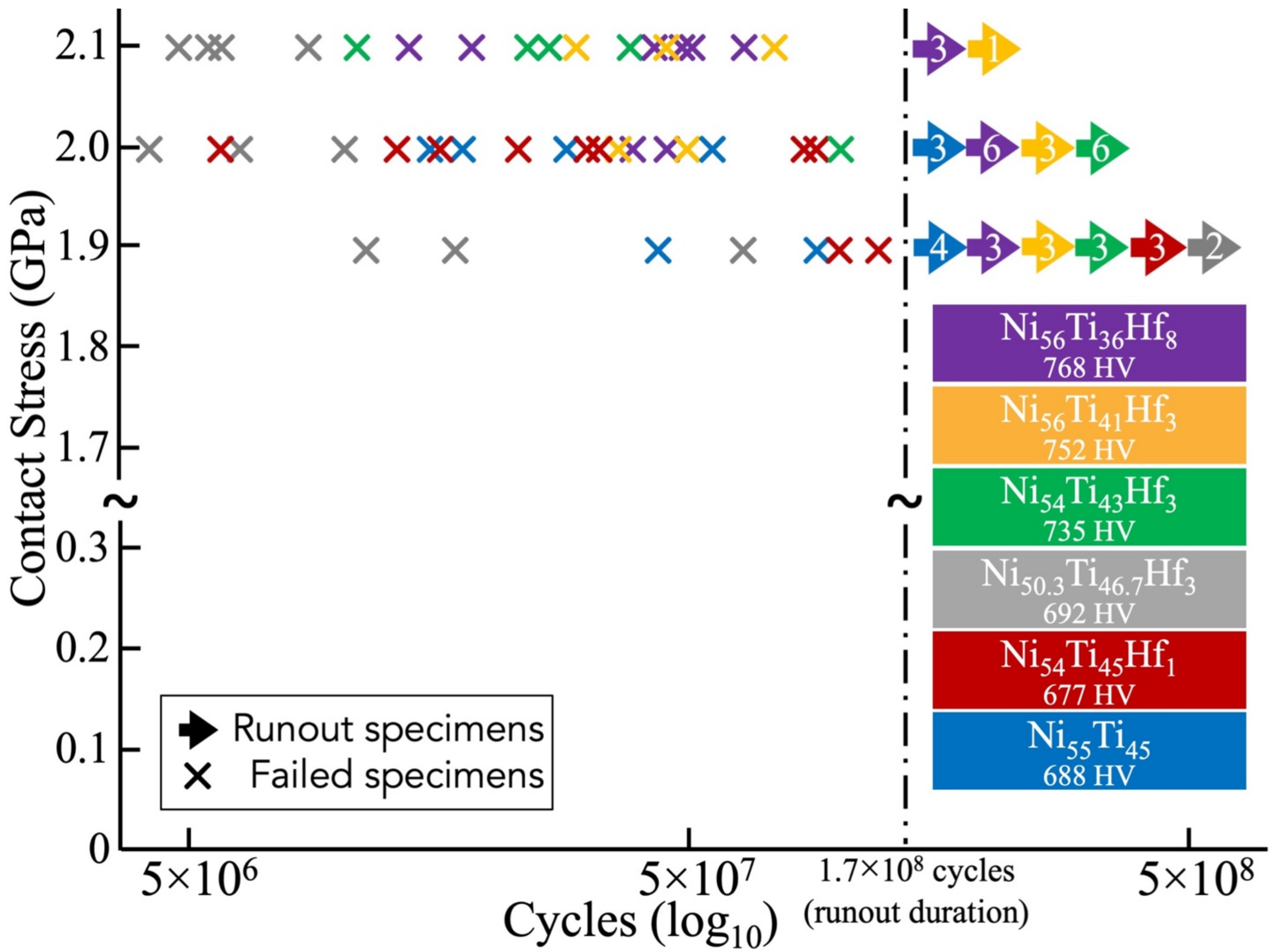
RCF testing results



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Microstructures of all RCF alloys

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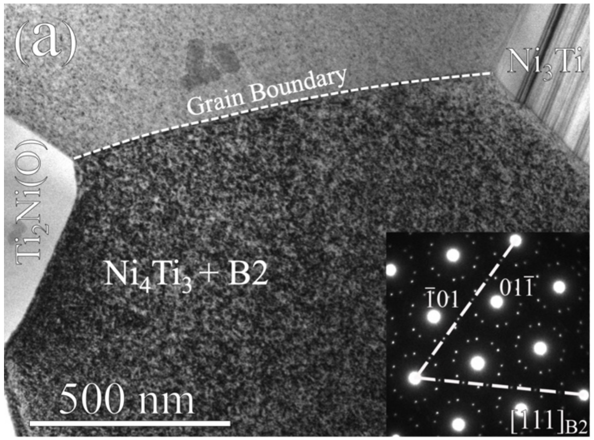
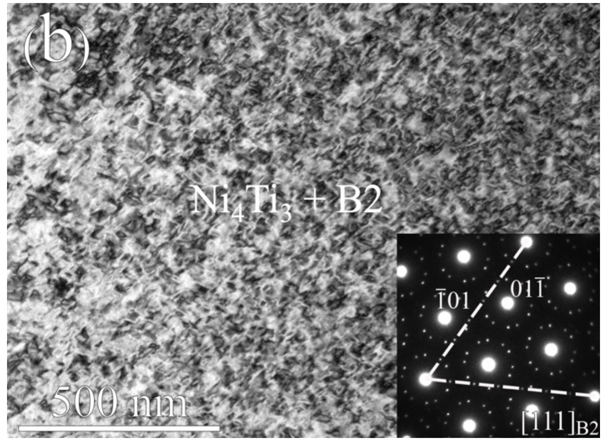
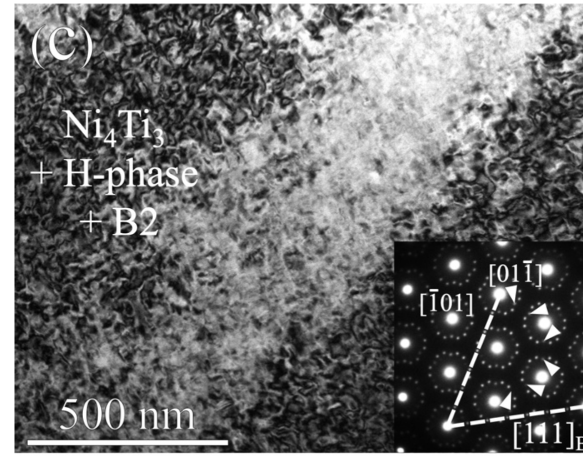
Baseline $Ni_{55}Ti_{45}$



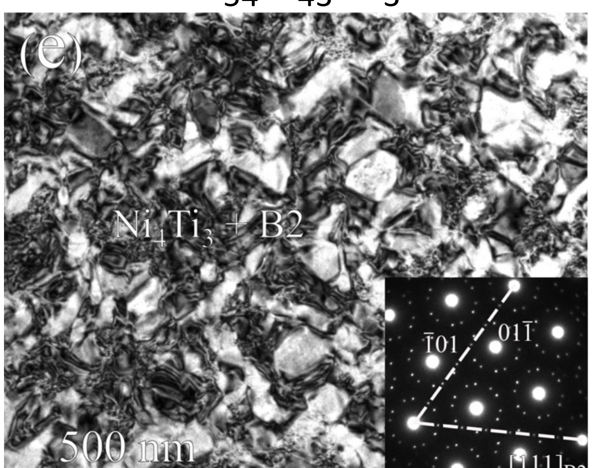
1st Gen $Ni_{54}Ti_{45}Hf_1$



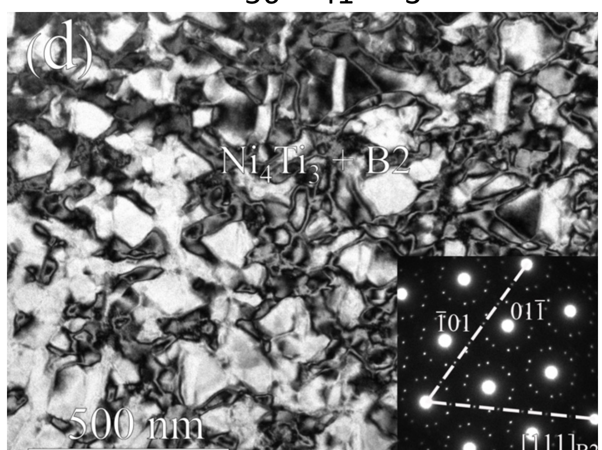
$Ni_{50.3}Ti_{46.7}Hf_3$



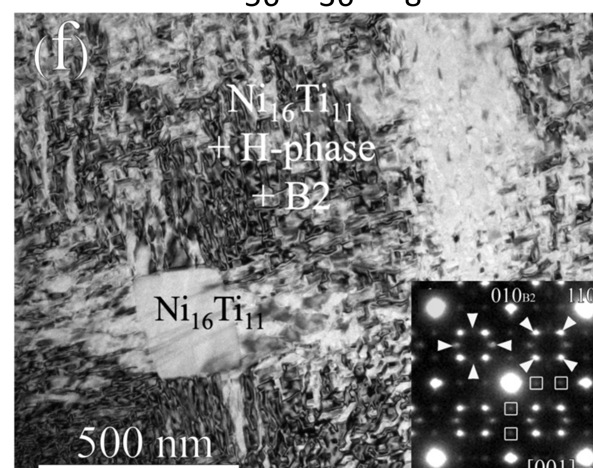
$Ni_{54}Ti_{43}Hf_3$



$Ni_{56}Ti_{41}Hf_3$



$Ni_{56}Ti_{36}Hf_8$



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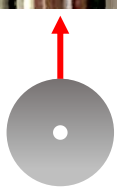
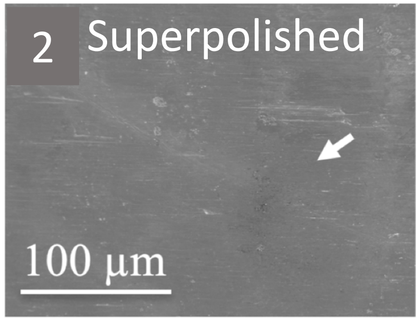
FIB lift-out samples made from RCF wear-tracks for 2 conditions

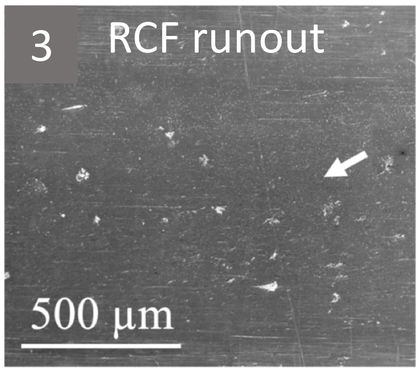
Used RCF rod

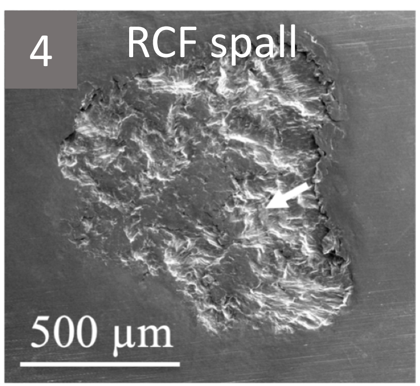
1



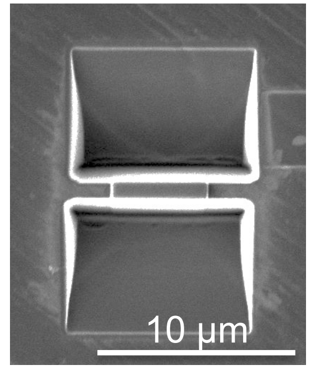
Electropolished 3mm disc

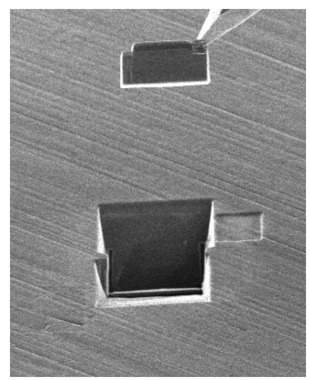


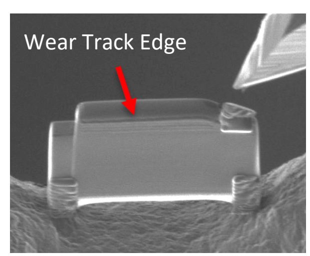




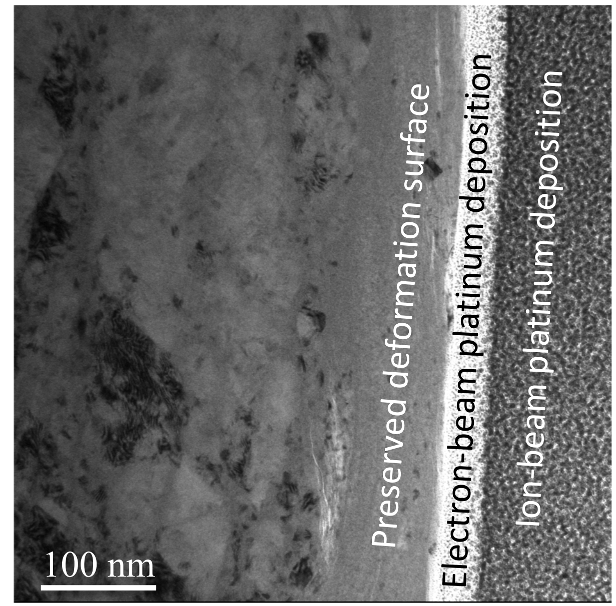
FIB foils taken directly from wear surface







BF-TEM and HR-TEM analysis of subsurface deformation



➔ First deposit electron-beam platinum deposition. Lower energy and protects the deformation surface

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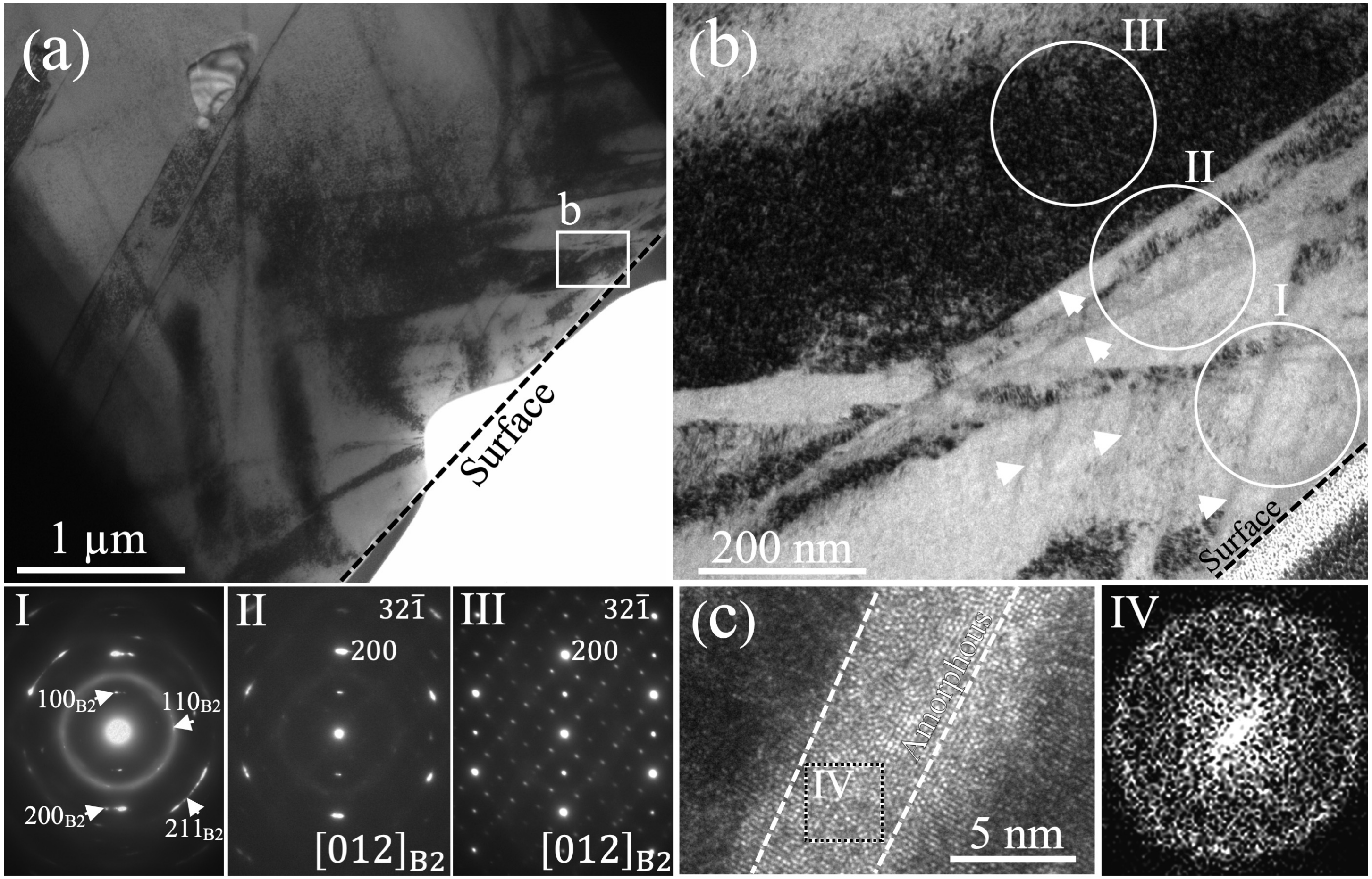
$Ni_{55}Ti_{45}$ Superpolished



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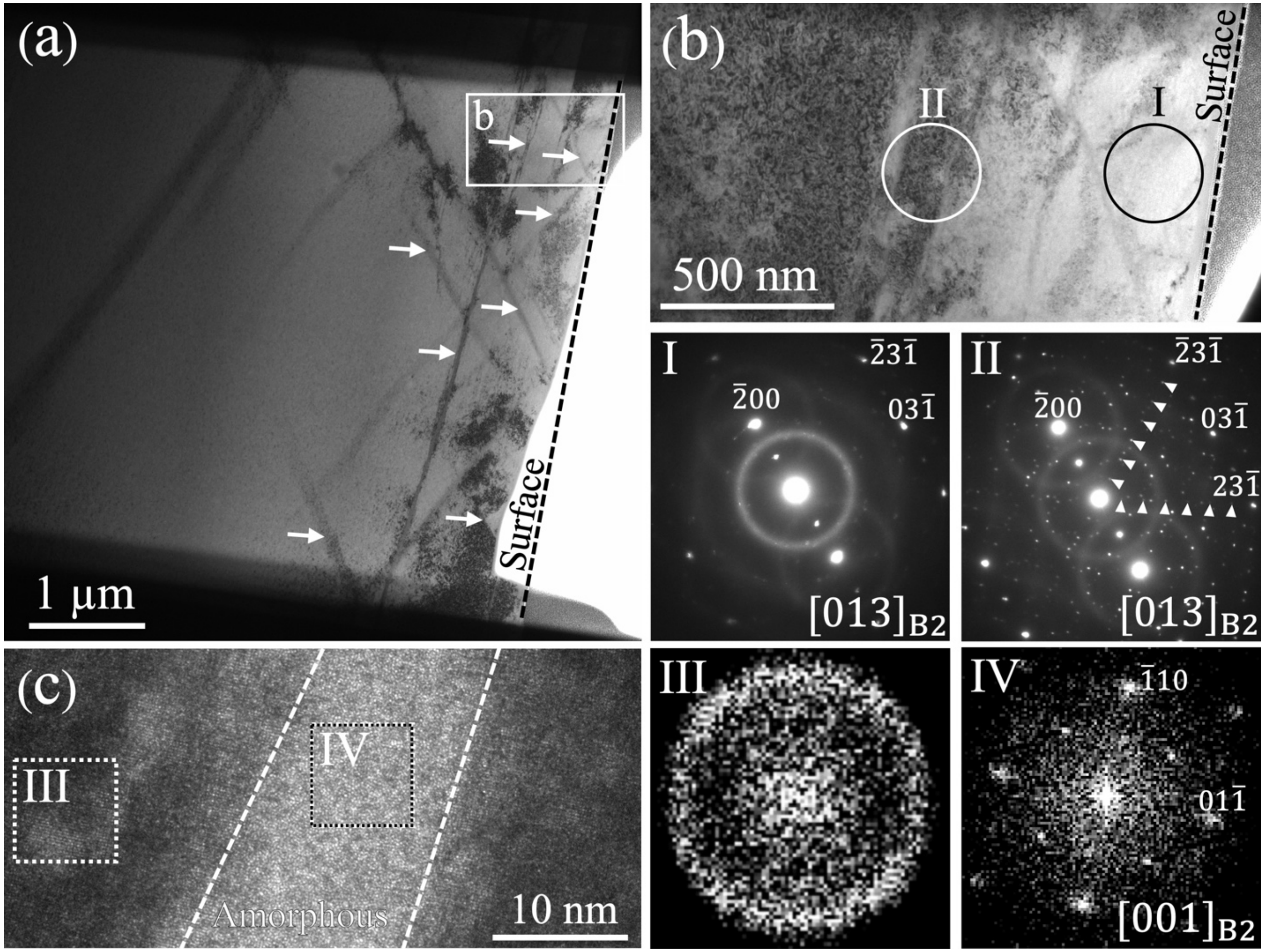
$Ni_{55}Ti_{45}$ RCF Runout



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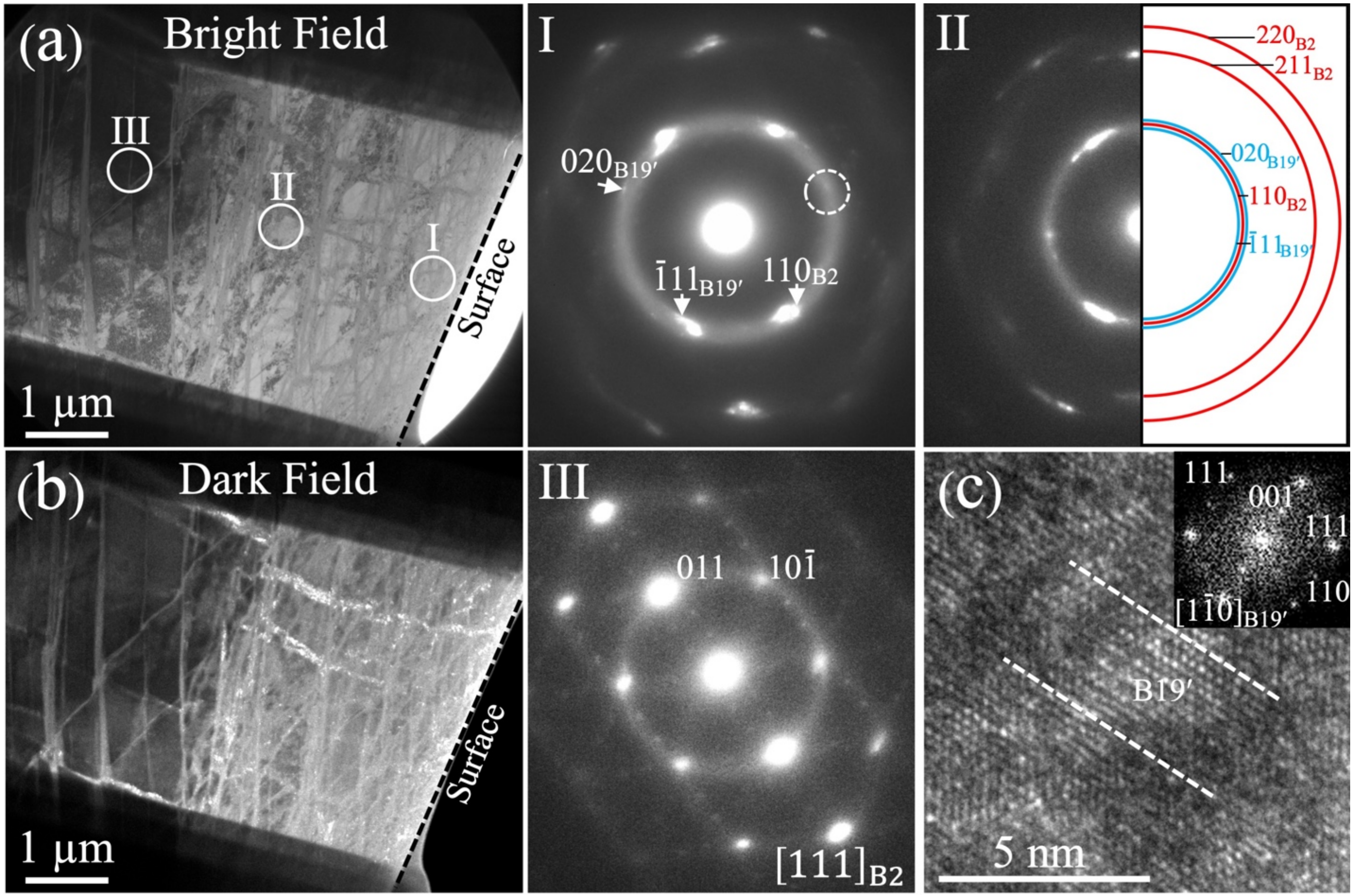
$Ni_{55}Ti_{45}$ RCF Spall



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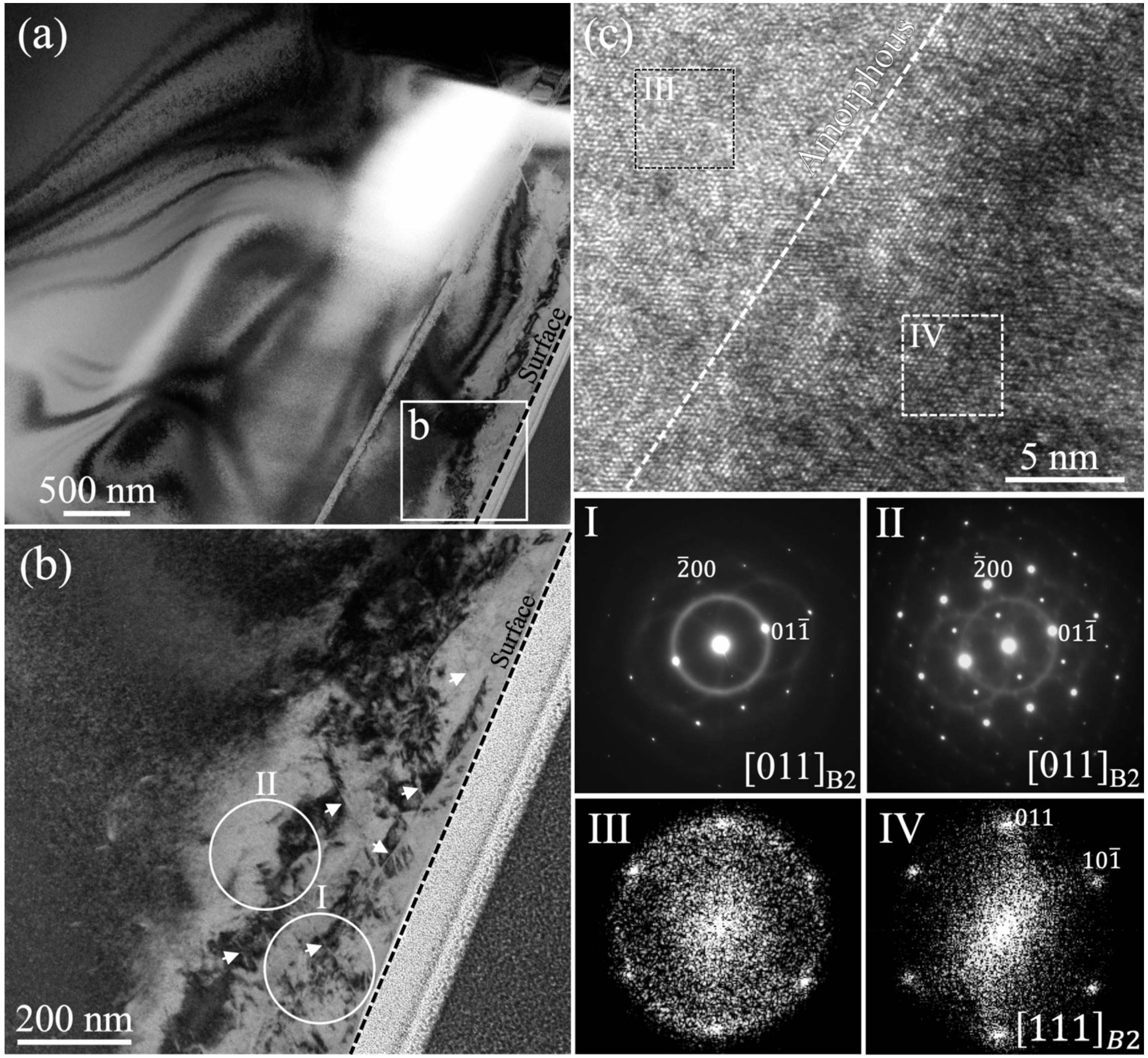
$Ni_{54}Ti_{45}Hf_1$ Superpolished



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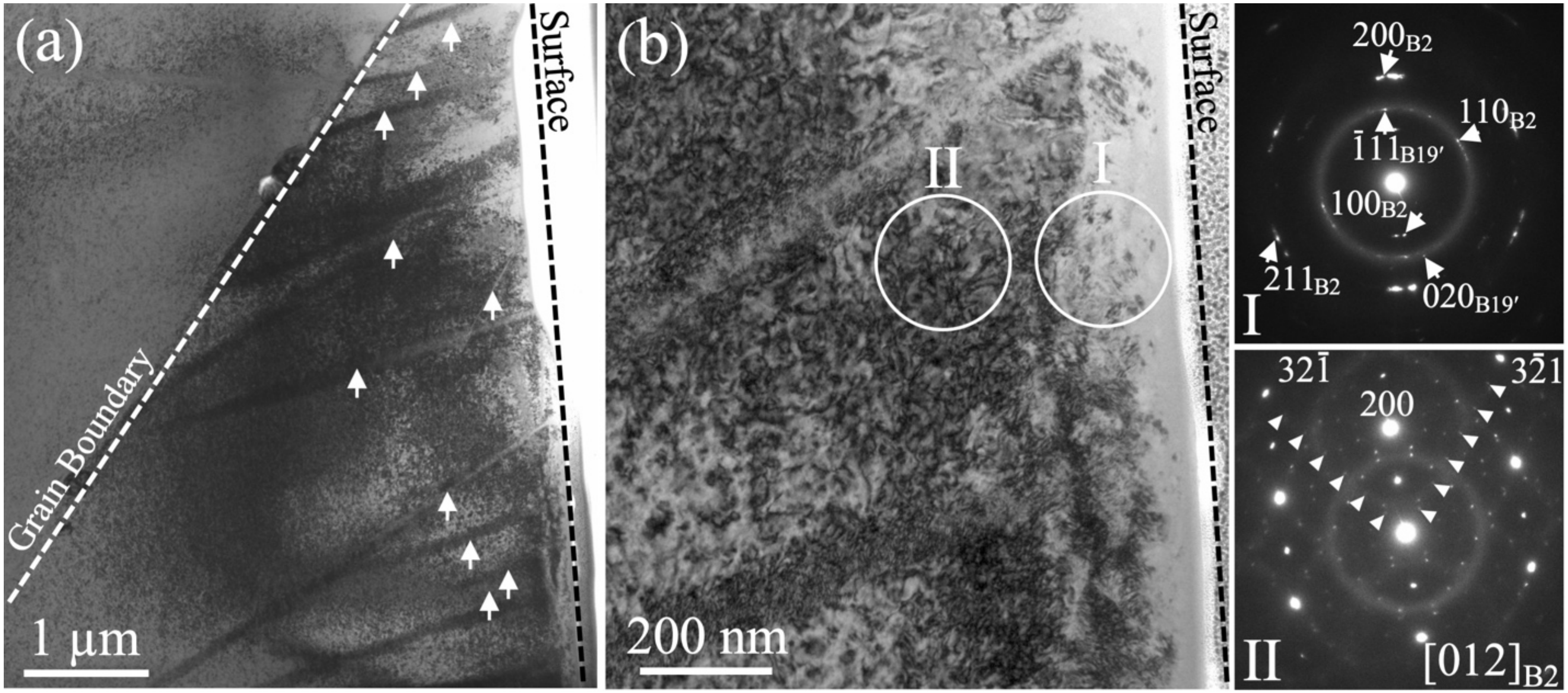
$Ni_{54}Ti_{45}Hf_1$ RCF Runout



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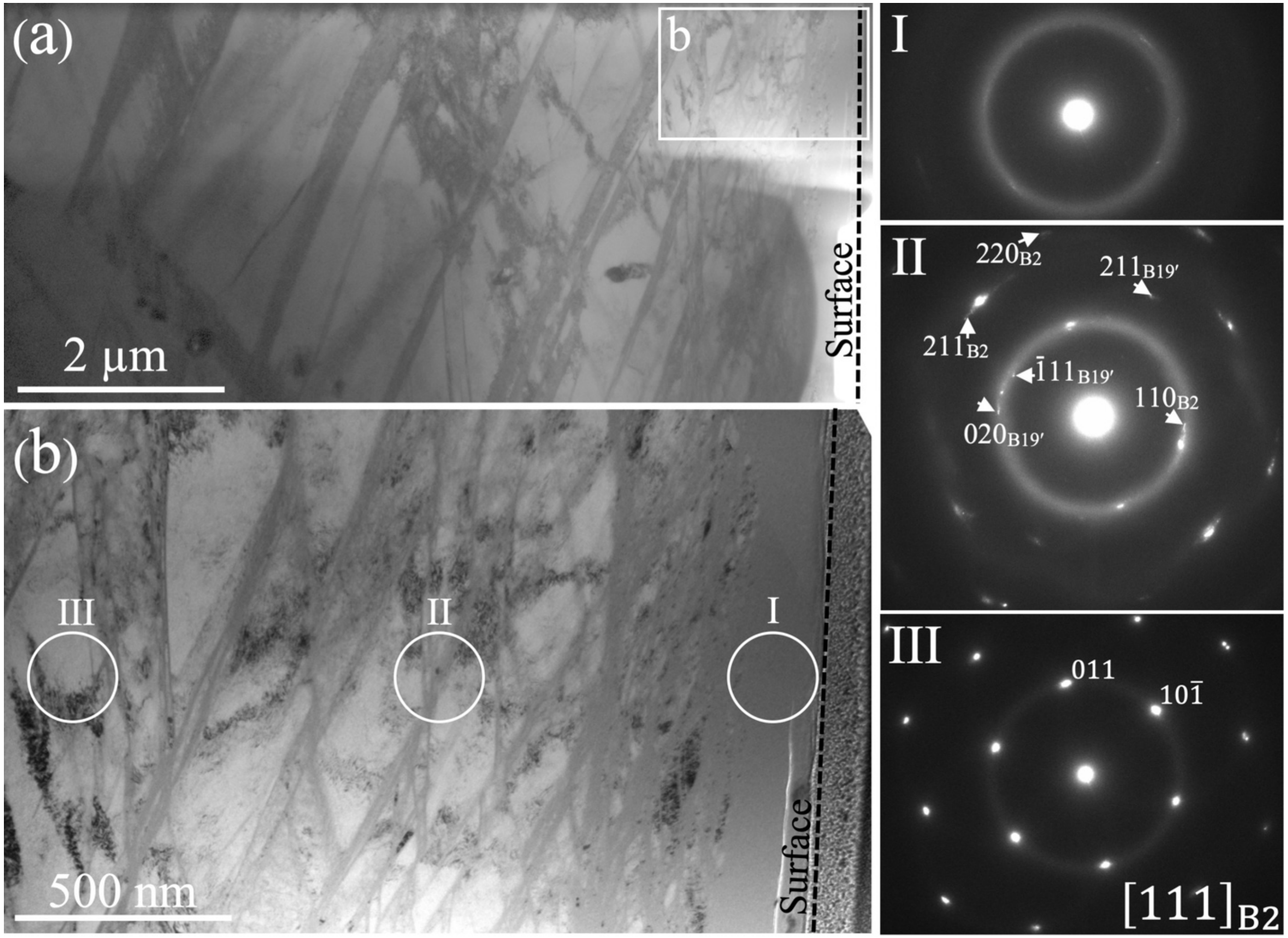
$Ni_{54}Ti_{45}Hf_1$ RCF Spall



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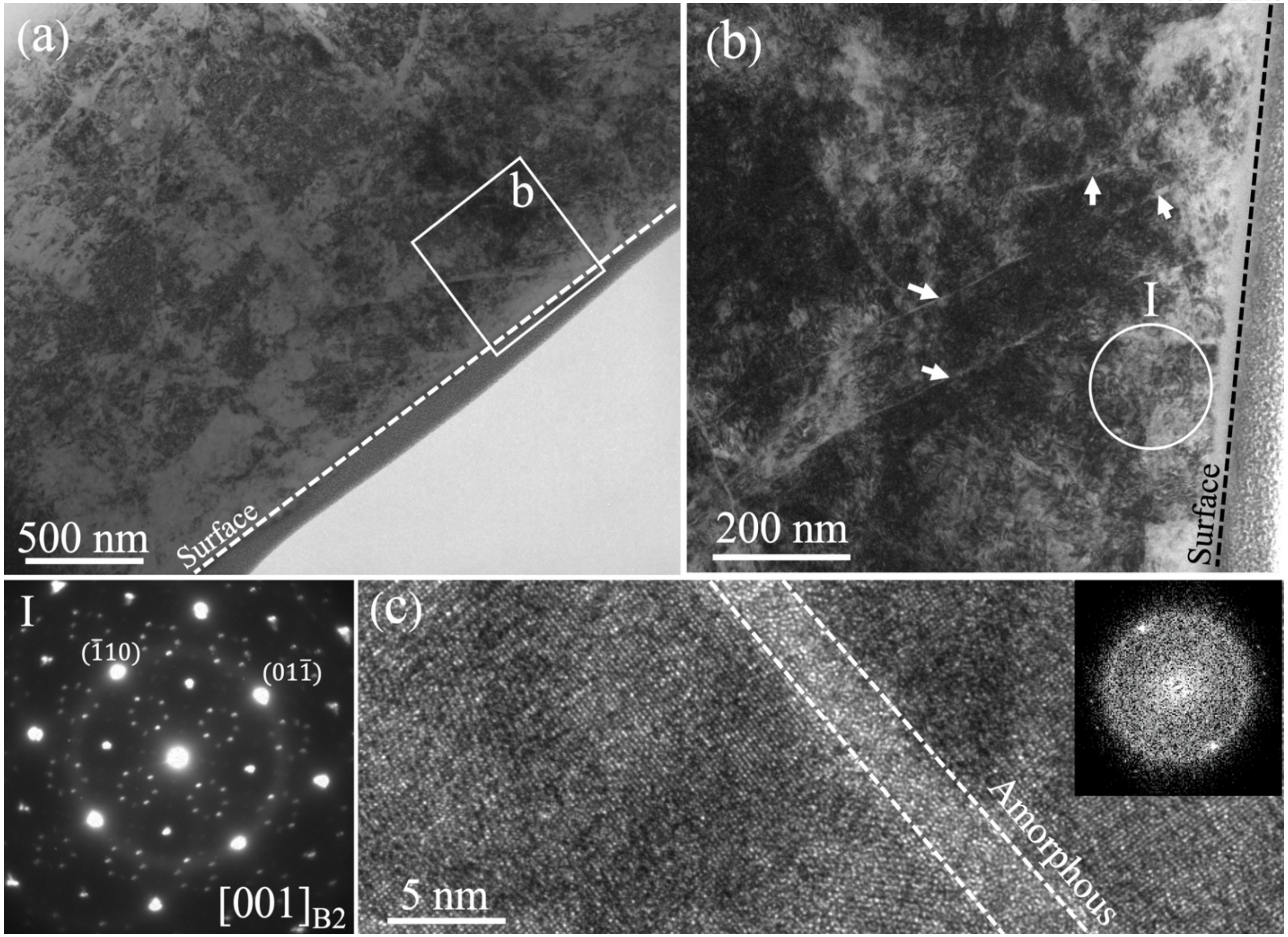
$Ni_{56}Ti_{36}Hf_{8}$ Superpolished



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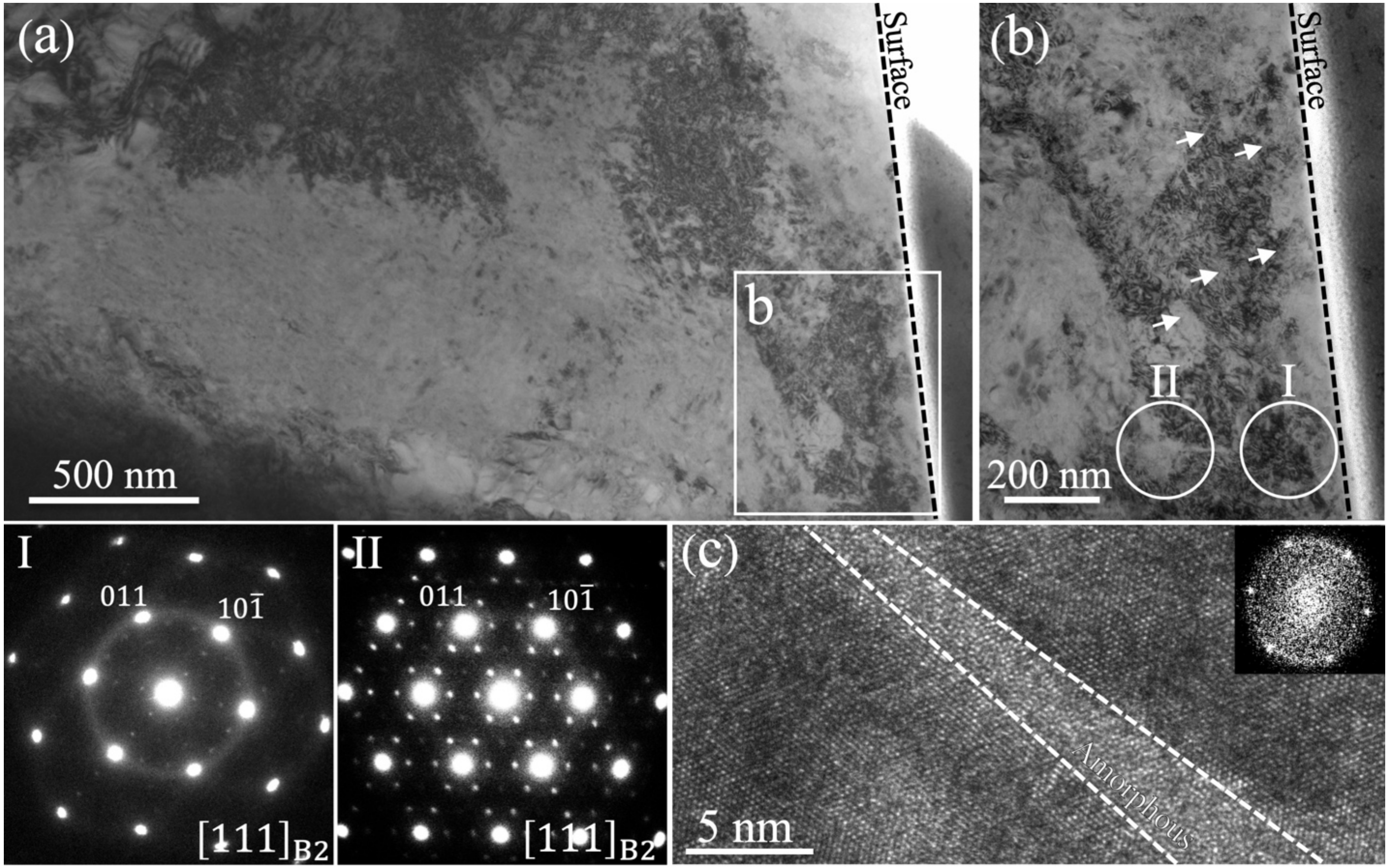
$Ni_{56}Ti_{36}Hf_8$ RCF Runout



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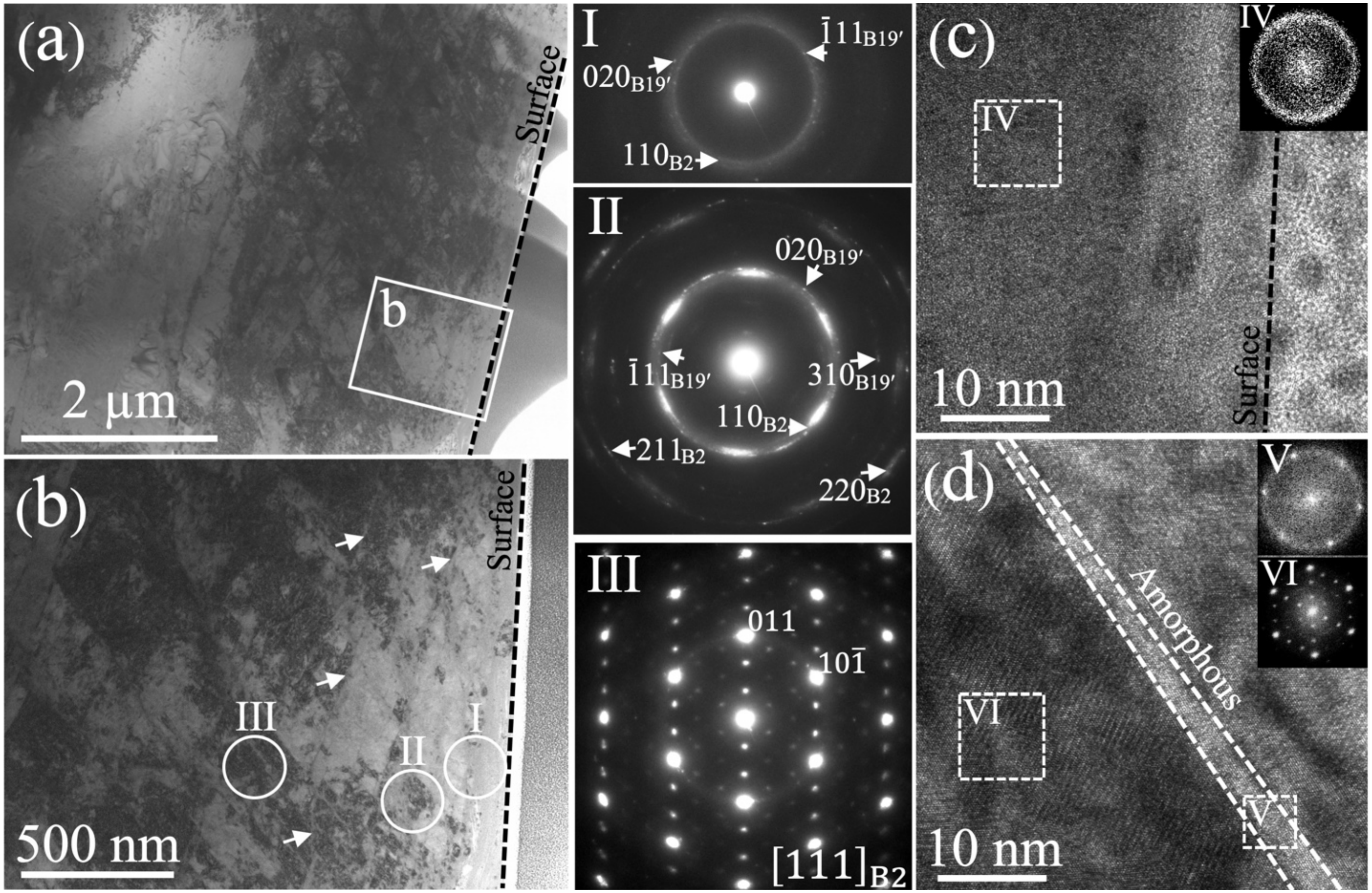
$Ni_{56}Ti_{36}Hf_8$ RCF Spall



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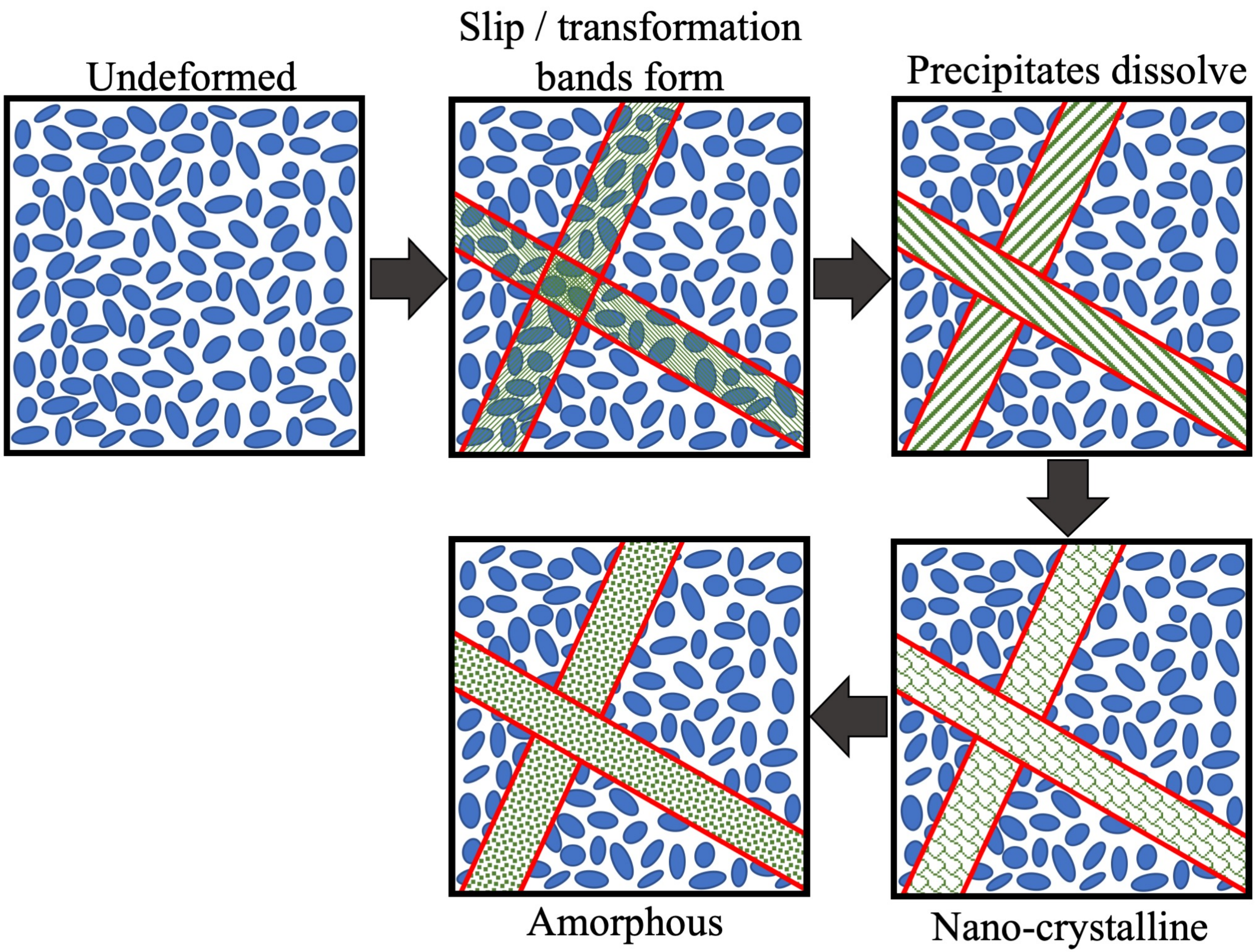
Deformation mechanism in NiTi and NiTiHf alloys under RCF



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Quantification of RCF samples

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	Dislocation Density ($10^{16}/m^2$)	Precipitation free zone	Deformation band width	Deformation band spacing	Amorphous region	Nano-crystalline region	Deformed region
Superpolish $Ni_{55}Ti_{45}$	6.2 ± 3	400	26 ± 9	123 ± 26			2 μm
Superpolish $Ni_{54}Ti_{45}Hf_1$	3.6 ± 2	375	21 ± 8	64 ± 12			1 μm
Superpolish $Ni_{56}Ti_{36}Hf_8$	8.5 ± 2	0	9 ± 5	259 ± 113			2 μm
RCF runout $Ni_{55}Ti_{45}$	11.9 ± 3	800	17 ± 9	79 ± 16			3 μm
RCF runout $Ni_{54}Ti_{45}Hf_1$	6.7 ± 3	350	32 ± 7	456 ± 122	50	50 – 100	3.5 μm
RCF runout $Ni_{56}Ti_{36}Hf_8$	16.8 ± 3	0	≤ 5	102 ± 36			
RCF spall $Ni_{55}Ti_{45}$	– –	4500			300	300 – 6000	
RCF spall $Ni_{54}Ti_{45}Hf_1$	– –	2000			300	300 – 2500	7 μm
RCF spall $Ni_{56}Ti_{36}Hf_8$	– –	400			100	100 – 500	0.5 μm

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Conclusions

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- Superpolishing produces amorphous bands in all conditions. Ni_4Ti_3 precipitates are dissolving close to the surface in $Ni_{55}Ti_{45}$ and $Ni_{54}Ti_{45}Hf_1$ alloys.
- Higher density amorphous bands are present in RCF runout condition that extend farther into the sample interior. B2 nano-crystal formation in $Ni_{55}Ti_{45}$ alloy. B2 and B19' nano-crystal formation in $Ni_{54}Ti_{45}Hf_1$ alloy. Precipitates are preserved in $Ni_{56}Ti_{36}Hf_8$ alloy.
- Spall conditions exhibit a graded microstructure. B2 and B19' nanocrystals are observed in all spall conditions. $Ni_{56}Ti_{36}Hf_8$ alloy restricts deformation to ~ 500 nm compared to ~ 5 µm for baseline alloy. Connected to resilient $Ni_{16}Ti_{11}$ and H-phase precipitates in this alloy.

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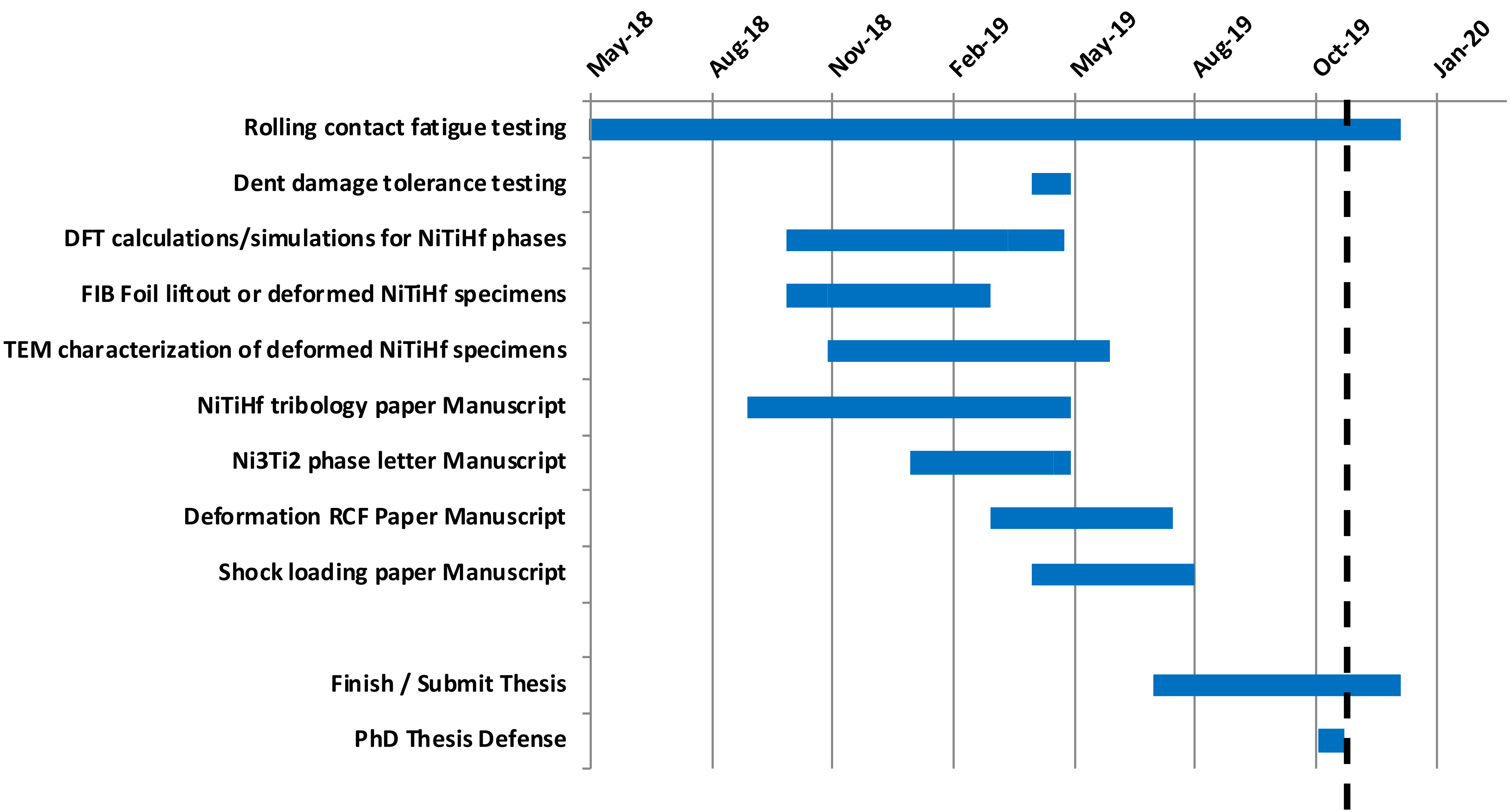
Progress



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Thank you very much!

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Acknowledgements:

Behnam Aminahmadi (Mines)
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Christopher Dellacorte (NASA GRC)
Ronald Noebe (NASA GRC)

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Center for Electron Microscopy and Analysis

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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

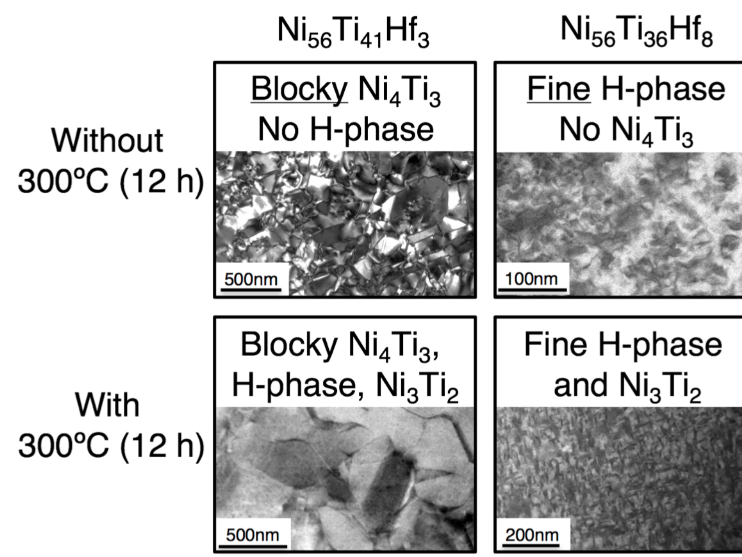
- Novel Ni-rich alloys provide ultra-hard optimized microstructures designed for space-age tribology applications.

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.



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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.

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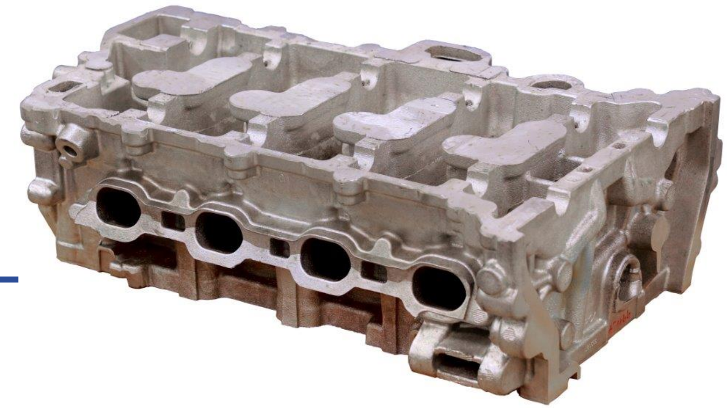
Project 29 - Identification of Deformation Mechanisms of Thermally Stable Cast Al-Cu Alloys via Neutron Diffraction and Creep Testing

Student: *Brian Milligan*

Faculty: *Amy Clarke*

Industrial Partners: *ORNL (Amit Shyam)*

Project Duration: *Sept. 2017 – May 2021*



Achievement

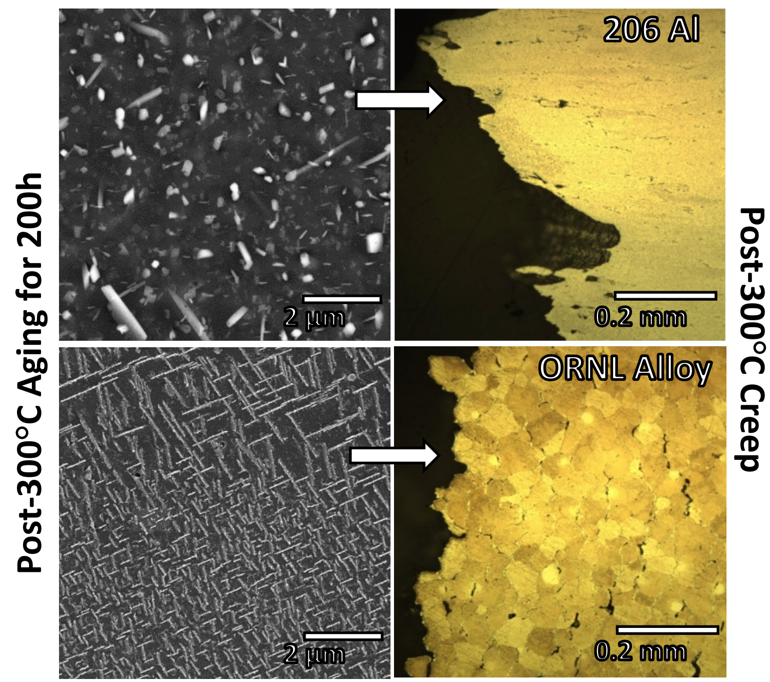
- Modeling of creep behavior in commercial and experimental Al-Cu alloys at high homologous temperature

Significance and Impact

- Thermally stable Al-Cu cylinder head alloys developed at ORNL outperform commercial alloys during creep loading, allowing for higher engine operating temperatures

Research Details

- Performed creep experiments and developed new low-stress microstructure-based creep model using results



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Project 29 - Identification of Deformation Mechanisms of Thermally Stable Cast Al-Cu Alloys via Neutron Diffraction

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Student: *Brian Milligan*

Faculty: *Amy Clarke*

Industrial Partners: *ORNL (Amit Shyam)*

Project Duration: *Sept. 2017 – May 2021*

Program Goal

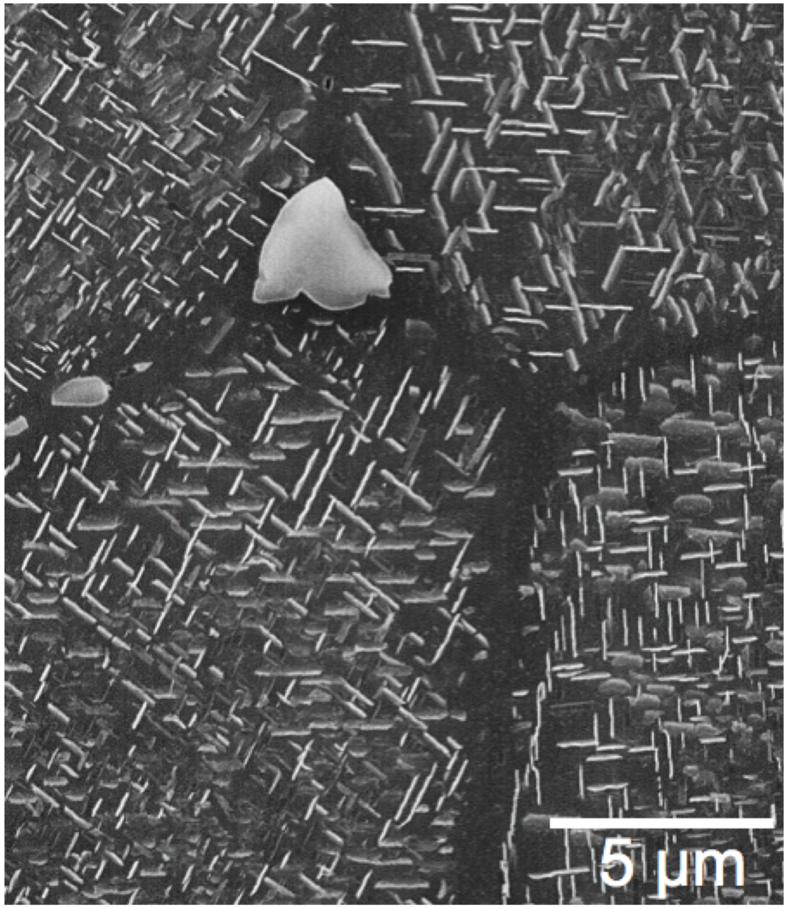
- Characterize the mechanical properties and microstructure of thermally stable Al-Cu alloys under various loading and aging conditions

Approach

- Utilize neutron diffraction, microscopy, and mechanical testing to identify deformation mechanisms ex-situ and in-situ

Benefits

- Improved scientific understanding of mechanical properties in Al-Cu alloys as well as insight into how to improve their performance at high temperature



Precipitation in RR350 aluminum alloy

Center Proprietary – Terms of CANFSA Membership Agreement Apply