Center for Advanced Non-Ferrous Structural Alloys

An Industry/University Cooperative Research Center

Project 17: Development of Advanced Nickel-Titanium-Hafnium Alloys for Tribology Applications

Spring 2018 Semi-Annual Meeting Colorado School of Mines, Golden, CO April 11-12, 2018

Student: Sean Mills (CSM) Faculty: Prof. Aaron P. Stebner (CSM) Industrial Mentor: Dr. Christopher Dellacorte (NASA GRC) Industrial Mentor: Dr. Ronald D. Noebe (NASA GRC)





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

 Student: Sean Mills (Mines) Advisor(s): Aaron Stebner (Mines) 	Project Duration PhD: August 2015 to August 2019
 <u>Problem:</u> 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. <u>Objective:</u> Elucidate the effect of Hf ternary alloying on metallurgy and bearing element performances. <u>Benefit:</u> 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. 	 <u>Recent Progress</u> Rolling contact fatigue (RCF) tests on Ni₅₄Ti₄₅Hf₁ and Ni₅₄Ti₄₃Hf₃ alloy specimens TEM characterization of microstructure evolution in 56at.% Ni alloys Continued Time/Temperature/Transformation (TTT) research

Metrics		
Description	% Complete	Status
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2. Literature review	80%	•
3. Rolling contact fatigue characterization of $Ni_{54}Ti_{45}Hf_1$ alloy	70%	•
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5. Alloy optimization – vary nickel and hafnium contents by 1-8 at%	20%	•

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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, hafniumenhanced 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.





OIntroduction

Why do we want to optimize Ni-Ti-Hf for space age bearings?

O Results

Rolling contact fatigue (RCF) testing

TEM microstructure analysis

O Conclusions

Optimized microstructure for best tribology properties.

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Application: Water recycling system on International Space Station



Nickel-rich Ni-Ti alloys show superior damage resistance

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Dent Resistance Load Capacity



Membership Agreement Apply

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

55at% NiTi in compression



Benafan et al. Intermetallics 2017





Casalena et al. Advanced Engineering Materials 2017

Ni-Ti has better corrosion resistance than steel, but susceptible to untimely failures

1 year of use in salt water

8

Ni₅₅Ti₄₅ (High Corrosion Resistance) Water Quenched NiTi



High Performance Steel (Low Corrosion Resistance)



Residual stresses lead to fracture post-machining

Small Hf substitution can lower solvus temp → reduction of residual stress Hf atoms substitute Ti atoms
 → slow kinetics while retaining hardness!

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





Optimized design space of Ni-Ti-Hf alloys



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¹⁰ Rolling contact fatigue testing of Ni₅₅Ti₄₅, Ni₅₄Ti₄₅Hf₁ and Ni₅₄Ti₄₃Hf₃



Spring loaded test head



Ball bearing retainer





Three ball-on-rod RCF test configuration



RCF Tests: Composition and secondary processing → better performance

11



Grain refinement shows no significant reduction of grain size at edge of spall

Used Ni-Ti-Hf test rod

IOWA STATE

12



Grain refinement shows no significant reduction of grain size at edge of spall

13



Fast fracture facets on edge of spall

Rolling Direction







Optimized design space of Ni-Ti-Hf alloys



¹⁶ More Hafnium rich compositions showed higher hardness



Microscopy focus on Ni₅₆Ti₄₁Hf₃ and Ni₅₆Ti₃₆Hf₈. Pre-aged specimens have higher hardness than non-pre-aged specimens.

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¹⁷ More Hafnium rich compositions showed higher hardness



¹⁸ EDS of light vs. dark regions in Ni₅₆Ti₄₁Hf₃ SHT_{WQ}

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Composition

Ni-Ti (Xat.%Ni, 1-Xat.%Ti)

Ni₄Ti₃ (57.1at.%Ni, 42.9at.%Ti)

Ni₃Ti₂ (60at.%Ni, 40at.%Ti)

Ni₃Ti (75at.%Ni, 25at.%Ti)

Ti₂Ni (66at.%Ni, 33at.%Ti)











Coarsening of Ni₄Ti₃. Not a significant change in microstructure compared to SHT_{wo} condition.



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²³ Ni₅₆Ti₄₁Hf₃ SHT_{WQ} + 300(12hrs)_{AC} + 550(1.5hrs)_{AC} Low Hf with pre-age shows blocky Ni₄Ti₃ structure and H-phase



²⁴ Ni₅₆Ti₄₁Hf₃ SHT_{WQ} + 550(4hrs)_{AC} Lower Hf without pre-age shows blocky Ni₄Ti₃





 Ni_4Ti_3 super-reflections fall under $\frac{1}{7}$

$$\frac{1}{7} < 321$$

682 HV





²⁵ Ni₅₆Ti₃₆Hf₈ SHT_{WQ}+ 300(12hrs)_{AC} + 550(4hrs)_{AC} Higher Hf with pre-aged condition shows fine Ni₄Ti₃ and H-phase



²⁶ Ni₅₆Ti₃₆Hf₈ SHT_{WQ}+ 550(4hrs)_{AC} Higher Hf without pre-age shows fine H-phase



Ni₅₆Ti₃₆Hf₈ SHT_{WQ} + 300(12hrs)+550(4hrs)



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Ni-Ti (Xat.%Ni, 1-Xat.%Ti)

Ni₄Ti₃ (57.1at.%Ni, 42.9at.%Ti)

Ni₃Ti₂ (60at.%Ni, 40at.%Ti)

Ni₃Ti (75at.%Ni, 25at.%Ti)

Ti₂Ni (66at.%Ni, 33at.%Ti)

Atomic-% (norm.)	Area	HAADF	Ti-KA	Hf-LA	Ni-KA
1	1258	28892	35.87	6.64	57.49
2	2279	29435	34.53	7.58	57.88
3	1280	30939	36.03	6.26	57.71
4	110	35935	36.80	8.37	54.83
5	100	34864	40.65	6.12	53.22
6	81	32784	37.00	7.64	55.36
7	81	29335	41.97	5.44	52.59
8	20433	21043	36.60	7.79	55.61
9	10176	46072	36.71	7.35	55.94

Large precipitate corresponds to Ni₄Ti₃ composition.

Center Proprietary – Terms of CANFSA Membership Agreement Apply

— 100 nm





²⁸ Secondary precipitation depends on composition and heat treatment

Without 300C (12hrs)



With 300C (12hrs)





²⁹ Secondary precipitation depends on composition and heat treatment



Preference for precipitation depends on Hf content Presence of both phases depends on pre-age





TTT data table for current alloys examined

Composition	Heat Treatment	TEM	DSC	Phase Information	Hardness (HV)
$\rm Ni_{50.3}Ti_{46.7}Hf_3$	SHT _{wq}		Yes	Νο	620.7
$\rm Ni_{50.3}Ti_{46.7}Hf_3$	SHT _{wq} + 300(12) _{AC}		Yes	Νο	630.3
$\rm Ni_{50.3}Ti_{46.7}Hf_3$	SHT _{WQ} + 550(4) _{AC}		Yes	Νο	586.2
$\mathrm{Ni}_{50.3}\mathrm{Ti}_{46.7}\mathrm{Hf}_{3}$	$SHT_{WQ} + 300(12)_{AC} + 550(4)_{AC}$	STEM	Yes	Fine H-phase, some Ni ₄ Ti ₃	676.2
$Ni_{56}Ti_{41}Hf_3$	SHT _{wq}	STEM,EDX	Yes	Light spherical features, no X.% disparity	706.5
$Ni_{56}Ti_{41}Hf_3$	SHT _{wq} + 300(12) _{AC}	HR-TEM	Yes	Blocky Ni ₄ Ti ₃	752.0
$Ni_{56}Ti_{41}Hf_3$	SHT _{WQ} + 550(4) _{AC}	TEM	Yes	Blocky Ni ₄ Ti ₃ , coarse martensite laths	661.6
$Ni_{56}Ti_{41}Hf_3$	$SHT_{WQ} + 300(12)_{AC} + 550(1.5)_{AC}$	HR-TEM,STEM,EDX	No	Blocky Ni_4Ti_3 , dispersed H-phase _(30nm)	657.4
$Ni_{56}Ti_{41}Hf_3$	$SHT_{WQ} + 300(12)_{AC} + 550(4)_{AC}$		Yes	No	709.8
$Ni_{56}Ti_{41}Hf_3$	$SHT_{WQ} + 300(12)_{AC} + 400(4)_{AC}$	HR-TEM	No	Blocky Ni_4Ti_3 , dispersed H-phase _(10nm)	698.6
Ni ₅₆ Ti ₃₆ Hf ₈	SHT _{wq}		Yes	Νο	716.3
$Ni_{56}Ti_{36}Hf_8$	SHT _{wq} + 300(12) _{AC}		Yes	Νο	705.4
$Ni_{56}Ti_{36}Hf_8$	SHT _{WQ} + 550(4) _{AC}	HR-TEM	Yes	Fine H-phase, heterogeneous $Ni_4Ti_{3(700nm)}$	700.0
Ni ₅₆ Ti ₃₆ Hf ₈	SHT _{wq} + 300(12) _{AC} + 550(4) _{AC}	STEM,EDX	Yes	Fine H-phase and Ni ₄ Ti ₃ , heterogeneous Ni ₄ Ti _{3(700nm)}	768.8
$Ni_{56}Ti_{36}Hf_8$	$SHT_{WQ} + 300(12)_{AC} + 400(4)_{AC}$	HR-TEM	No	Fine H-phase	692.0
Ni ₅₆ Ti ₃₆ Hf ₈	$SHT_{WQ} + 300(12)_{AC} + 400(1.5)_{AC}$		No		726.5





Conclusions for Ni-Ti-Hf

- Pre-aging without additional treatment does not show H-phase, only Ni₄Ti₃.
- Existence of interface within large Ni₄Ti₃ precipitates. Includes misfit dislocations.
- Increase in Hf from 3at.% to 8at.% under same aging conditions shows suppressed nucleation and growth of Ni₄Ti₃ precipitation.
- Preference between Ni₄Ti₃ and H-phase switches when Hf content is increased.
- Large heterogeneous formation of $Ni_4Ti_{3-x}Hf_x$ exists in 8at.%Hf samples.







Future work for Ni-Ti-Hf

- Combine rolling contact fatigue with microstructure analysis and develop time/temperature/transformation to determine optimized alloy composition and heat treatment.
- Perform rolling contact fatigue on higher hardness alloys to confirm that higher hardness leads to better fatigue performance.
- Acta. Mat. paper on Ni-Ti-Hf microstructural optimization for tribology.





Gantt Chart

						2018						
me		Begin da	. End da	lovember	l December	January	l February	l March	l April	May	June	l July
0	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	_		_	٦					
	 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	_							٦	
	 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									
								Dro	cont			

Present







Thank you

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35

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

Graduate Student – Sean Mills (CSM) Faculty/Advisors – A.P. Stebner (CSM) Industrial Mentors – C. DellaCorte & R.D. Noebe (NASA Glenn)

Program Goal

Development of Ni-Ti-Hf alloys with high strength, hardness and toughness via superelasticity

Approach

Characterize residual stress and fatigue properties of Ni-Ti with added levels of Hf

Correlate properties to microstructural variations between alloys

Benefits

A new class of bearing materials with high strength and high damage tolerance

Project Duration

Aug. 2015 to Aug. 2019

Previous rolling contact fatigue tests

Test Date	2/16	3/16	4/16	5/16	6/16	7/16	8/16	9/16	10/16
Sample Composition	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$
Secondary Processing	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age
Stress (GPa)	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.8	1.8
Lifespan (10 ⁸ cycles)	.33	>1.7	>1.7	>1.7	>1.7	>1.7	>1.7	1.47	>1.7
Test Date	8/16	9/16	11/16	11/16	12/16	1/17	2/17	3/17	3/17
Sample Composition	$Ni_{54}Ti_{45}Hf_1$	Ni ₅₄ Ti ₄₅ Hf ₁	$Ni_{54}Ti_{45}Hf_1$						
Secondary Processing	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age	1000C _{AC} + 400C Age
Stress (GPa)	1.9	1.9	2.0	2.0	2.0	1.9	1.9	1.9	1.9
Lifespan (10 ⁸ cycles)	.12	.31	.08	.22	.48	1.2	1.32	1.28	>1.7
Test Date	2/17	2/17	4/17	4/17	5/17	5/17			
Sample Composition	$Ni_{54}Ti_{45}Hf_1$	Ni ₅₄ Ti ₄₅ Hf ₁	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	Ni ₅₅ Ti ₄₅	Ni ₅₅ Ti ₄₅			
Secondary Processing	900C _{WQ} +400C Age	900C _{WQ} +400C Age	900C _{AC} +400C Age	900C _{AC} +400C Age	1000C _{WQ} +400C Age	1000C _{WQ} +400C Age			
Stress (GPa)	1.9	1.9	1.9	1.9	1.9	1.9			
Lifespan (10 ⁸ cycles)	>1.7	>1.7	>1.7	1.18	>1.7	>1.7			

Current rolling contact fatigue tests

Test Date	7/17	8/17	8/17	9/17	9/17	11/17	12/17	1/18	1/18
Sample Composition	$Ni_{54}Ti_{45}Hf_1$	$\rm Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$
Secondary Processing	1000C _{AC} + 400C Age	1000C _{wq} + 400C Age	1000C _{WQ} + 300C(12hrs) _{AC}	1000C _{WQ} + 300C(12hrs) _{AC}	1000C _{WQ} + 300C(12hrs) _{AC}				
Stress (GPa)	2.0	2.0	2.0	2.0	2.0	1.9	1.9	2.0	2.0
Lifespan (10 ⁸ cycles)	.33	.94	.74	.72	.36	>1.7	>1.7	>1.7	>1.7

Test Date	2/18	2/18
Sample Composition	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$
Secondary Processing	1000C _{WQ} + 300C(12hrs) _{AC}	1000C _{WQ} + 300C(12hrs) _{AC}
Stress (GPa)	1.9	2.0
Lifespan (10 ⁸ cycles)	>1.7	.81

