17. DEVELOPMENT OF ADVANCED NICKEL-TITANIUM-HAFNIUM ALLOYS FOR TRIBOLOGY APPLICATIONS

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17.1. Project Overview and Industrial Relevance

The high hardness, high compressive elastic strength and good corrosion resistance of ternary Ni-Ti-Hf alloys makes them optimum candidates for specialized bearing applications. In addition, aged NiTiHf alloys exhibit superelastic hysteresis curves under compressive loading and in torsion as shown in **Fig. 17.1**. Conventional superelastic Ni-Ti alloys are known to experience high hardness and high residual stresses upon rapid quenching, resulting in cracking and machining distortion, whereas they have low hardnesses if cooled slowly. This project is designed to elucidate the effects of hafnium additions on the structure and properties of Ni-Ti-Hf alloys with an emphasis on bearing element performance. It will be shown that hafnium additions have a significant impact on the transformation kinetics, which results in reduced residual stresses while retaining the high strength and hardness that are desirable for bearing applications.

This multimodal study will include rolling contact fatigue characterization, residual stress and hardness calculation and time/temperature/transformation studies of certain NiTiHf alloys. Alloy optimization will be conducted by varying the nickel and hafnium contents by 1-8 at. %. **Fig. 17.2** outlines the design space of the project that shows the varied nickel and hafnium contents of the samples that will be investigated in the future. The sample compositions that have been tested in rolling contact fatigue are highlighted and the sample compositions that have been investigated via TEM methods are highlighted. Likely outcomes to the study include further understanding of rolling contact fatigue performance, failure mechanisms, performance (hardness, strength, life) versus residual stresses, and a map of alloy design space to allow optimization of NiTiHf systems for tribology applications.

17.2. Previous Work

17.2.1. Rolling Contact Fatigue

It is known that for nickel-rich compositions of NiTi, and also ternary NiTiHf compositions with very low amounts of hafnium (~ 1 at. %), the Ni_4Ti_3 phase may be used for precipitation hardening without compromising the high hardness of the solid solution. In fact, the precipitates can also increase the hardness of the alloys. However, for NiTiHf with greater amounts of Hf (8 at. % or more), Hf and Ni rich "H-phase" precipitates form instead of Ni_4Ti_3 and provide even greater strengthening. ***Therefore, it is hypothesized that H-phase precipitation can also provide superior hardness to alloys, resulting in superior wear performance in rolling contact fatigue (RCF).*** Testing of NiTiHf samples using a three ball-on-rod set-up is imperative to ensuring this hardening behavior improves the component from an engineering standpoint.

A significant reduction in rolling contact fatigue performance has been observed in the $Ni_{54}Ti_{45}Hf_1$ alloy between 1.9 and 2.0 GPa. The brittle nature of spalling failures that are common in the specimens that failed at 2 GPa provide insight to the dominant failure mechanisms under Hertzian contact conditions. ***Specifically, it was speculated that there must be a change in the uniaxial stress-strain behavior (for instance, the critical stress for martensite formation) in the range of 1.9-2.0 GPa that can be related to rolling contact fatigue performance.*** Thus, performing uniaxial compression testing on the same material as tested under RCF conditions was conducted in order to provide insight into the relationship between the critical contact stresses under fatigue conditions and the distinctive features on the stress-strain curves. Current long-term RCF test results can be viewed in **Table 17.1**.

17.2.2. SEM and Optical Characterization

SEM analysis of failed wear tracks was conducted to determine the failure mechanism, intensity of failure and approximate failure location. A common type of failure in NiTi alloys is fatigue spalling on the surface of the material. ***To what extent does the material plastically deform and what are the damage mechanisms under the wear track in association with failure?*** Determining the evolution of damage in association with the wear tracks is needed. Center vs. edge comparison and surface vs. bulk comparison are natural approaches to ascertain differences between subsurface deformation zones for "unfailed" wear tracks versus spalled wear track regions. However, this needs to be done in such a way to cover large sample volumes effectively. Preparing polished surfaces through the wear tracks, both perpendicular and parallel to the rod axis, will enable the use of EBSD to determine substructure including any evidence for sub-grain rotations using, for example, grain reference orientation maps. Another possible technique to apply is electron channeling contrast imaging (ECCI) of defect structures which may reveal the damage evolution from the wear track surface to the bulk. In this way, a much larger area can be mapped out than is possible with TEM in order to get a better sense of what deformation processes are occurring in rolling contact fatigue. This may help determine the spatial distribution of damage with respect to its location and orientation within the wear track on a length scale that is suitable to the sample. FIB extraction of samples and TEM analysis for higher resolution can also be performed as needed to confirm the details of the remnant deformation.

17.3. Recent Progress

17.3.1. Rolling Contact Fatigue

Continued work on $Ni_{54}Ti_{45}Hf_1$ alloys has been performed which reveals a consistent failure of the alloy at 1.9-2.0 GPa. When compared with the binary $Ni_{55}Ti_{45}$ system under water quenching conditions, the air-cooled ternary alloy specimens are superior. However, when $Ni_{54}Ti_{42}Hf_3$ is considered under water quenching conditions, the samples were successfully running to completion (1.7E8 cycles) at both the 1.9 and 2.0 compressive stress levels. The improvement in fatigue performance is indicative that compositional adjustments (increasing hafnium levels slightly) and secondary processing (water quenching with additional aging treatment) play an important role in the longevity of the rolling contact fatigue specimens under higher compressive loads.

17.3.2. TEM Characterization of 56 at. % nickel alloys

NiTiHf alloys with target compositions of $Ni_{56}Ti_{41}Hf_3$ and $Ni_{56}Ti_{36}Hf_8$ were made by induction-melting high-purity elemental constituents using a graphite crucible and casting into a copper mold. The ingots were homogenized in vacuum at 1050 ºC for 72 h and then extruded at 900 ºC at a 7:1 area reduction ratio. The extruded rods were sectioned into samples that were initially solution annealed at 1050 ºC for 30 minutes and water quenched. Samples of each composition were then pre-aged at 300 ºC for 12 h and air cooled, and finally aged a second time at 500 ºC for 4 h and air-cooled. To isolate the effect of pre-aging on the functional properties of NiTiHf alloys, other test samples were directly aged at 550 ºC for 4 h after the solution-anneal treatment (without pre-aging at 300 ºC for 12 h). Conventional and high-resolution transmission electron microscopy (HRTEM), bright-field transmission electron microscopy and selected area electron diffraction microscopy of aged NiTiHf samples was carried out using an FEI Talos TEM (FEG, 200 kV). The TEM foils were prepared by electropolishing at an electrolyte of 30 vol. % HNO_3 in methanol at around −35 ºC. To measure the size of H-phase and Ni_4Ti_3 precipitates, and collect information on precipitate morphology, several HRTEM taken from various regions were used. A probe-corrected FEI Titan 1 was employed to take atomic resolution scanning transmission electron microscopy (HR-STEM) images of some of the microstructures. Digital Micrograph was utilized to extract diffraction information of precipitates analyzed in the HRTEM and HR-STEM images collected.

Findings through these techniques indicate a significant change in microstructure and material properties by adjustments in composition and secondary processing. The effect of hafnium shows a direct change in preference from one secondary precipitation type to another. **Fig. 17.3** below clearly shows the change in morphology with respect to composition and aging conditions. At 3 at. % Hf levels, preference for blocky Ni_4Ti_3 precipitation was observed whereas at 8 at. % Hf, preference for fine H-phase precipitation led to higher strength and toughness. The effect of secondary processing via multi-step heat treatments show a change in the precipitates formed in a given sample. A two-step heat treatment of firstly, solution heat treatment and water quenching and then a secondary aging step at 550 ºC before air-cooling produced only one precipitate type in the material. When an intermediate heat treatment step of 300 ºC for 12 h is added to the secondary processing steps, there are both significant quantities of Ni_4Ti_3 and H-phase present within the microstructure. As a result, the interaction between the two strengthening precipitates hardens the material relative to when only one of the precipitate types is present. These two parameters have a significant effect on the overall rolling contact fatigue performance of the material and are important steps leading up to determination of the optimized microstructure for tribology.

17.4 Plans for Next Reporting Period

- Continued work aimed at improving the rolling contact fatigue tests.
- Continued characterization of 50-56 at. % Ni and 3-8 at. % Hf compositions for various heat treatments.
- Multi-technique TTT mapping through the use of TEM techniques and SAXS/WAXS techniques to help develop a better understanding for the NiTiHf system.

17.5. References

1) Dellacorte, Christopher, Malcolm K. Stanford, and Timothy R. Jett. "Rolling Contact Fatigue of Superelastic Intermetallic Materials (SIM) for Use as Resilient Corrosion Resistant Bearings." Tribology Letters 57.3 (2015): 1-10.

2) Hornbuckle, B. C., R. D. Noebe, and G. B. Thompson. "Influence of Hf solute additions on the precipitation and hardenability in Ni-rich NiTi alloys." Journal of Alloys and Compounds 640 (2015): 449-454.

3) Otsuka, Kazuhiro, and Xiabing Ren. "Physical metallurgy of Ti-Ni based shape memory alloys." Progress in materials science 50.5 (2005): 511-678.

17.6. Figures and Tables

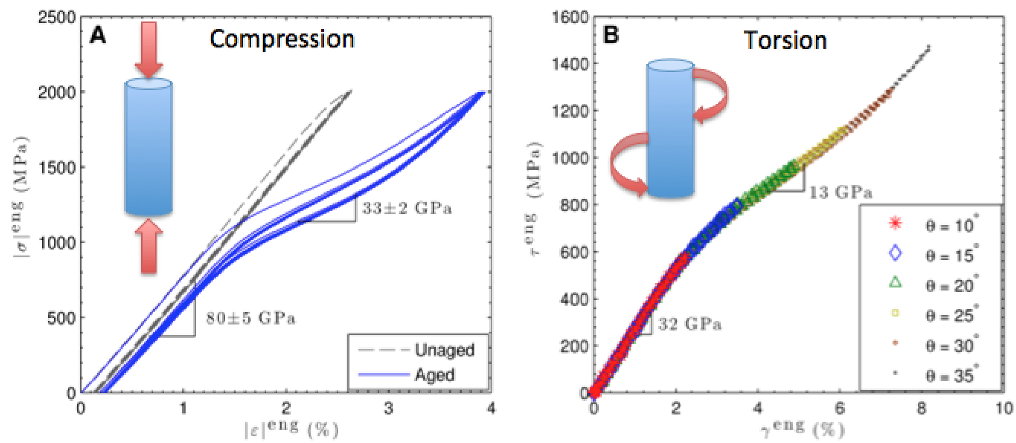

Figure 17.1: Superelastic hysteresis curves for aged NiTiHf under compressive loading and aged NiTiHf under torsional loading.

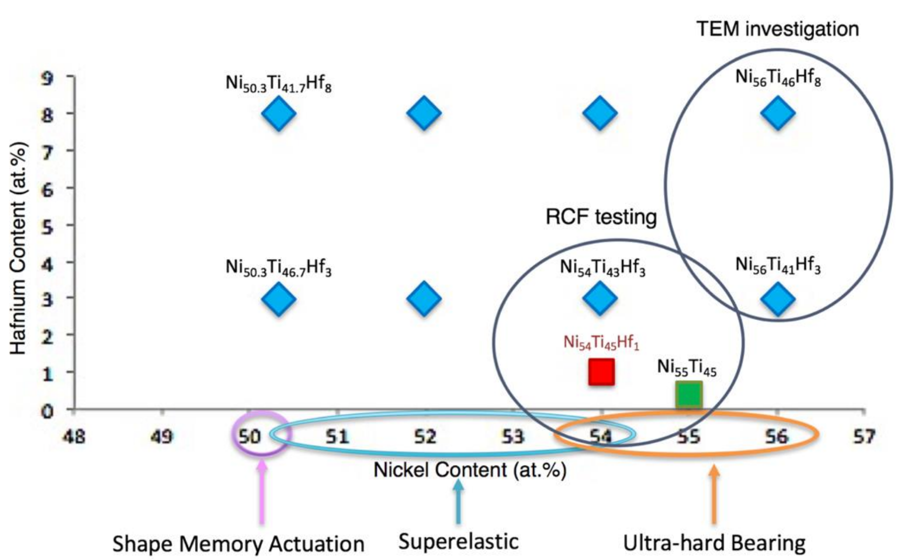

Figure 17.2: Design space of NiTiHf alloys. CSM1–CSM8 samples vary in nickel and hafnium content. Their applicability as SMAs, superelastic alloys, and bearing alloys are listed.

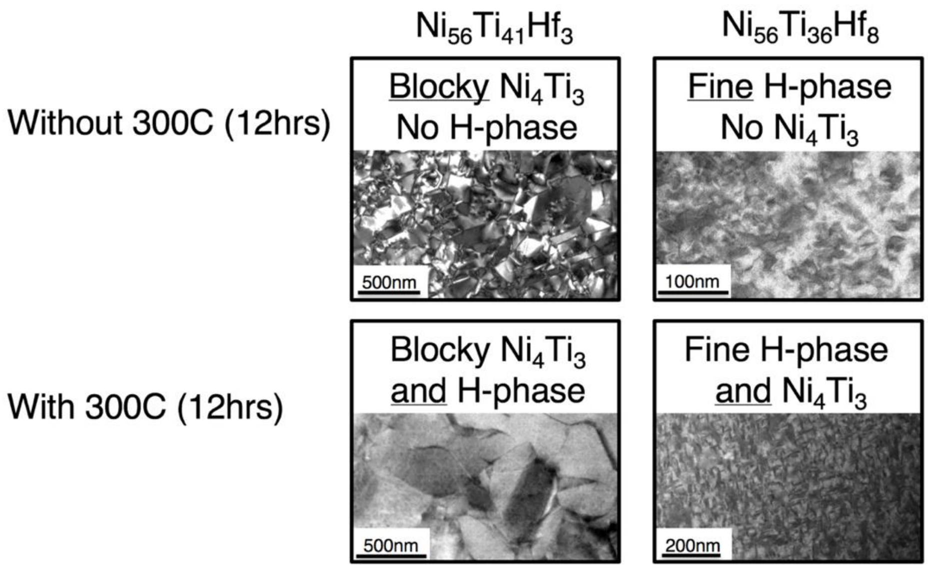

Figure 17.3: The preference for the type of secondary precipitation in Ni-rich NiTiHf alloys depends on changes in hafnium content and heat treatment. In order for both secondary precipitates to form within the microstructure a 300ºC(12h) pre-age is necessary.

Table 17.1: Rolling contact fatigue test results.

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	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$
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)	1.9	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

Test Date	7/17	8/17	8/17	9/17	9/17	11/17	12/17	1/18	1/18
Sample Composition	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{45}Hf_1$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$	$Ni_{54}Ti_{43}Hf_3$
Secondary Processing	$1000C_{AC}$+ 400C Age	$1000C_{AC}$+ 400C Age	$1000C_{AC}$+ 400C Age	$1000C_{AC}$+ 400C Age	$1000C_{AC}$+ 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