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Effect of a pre-aging treatment on the mechanical behaviors of $Ni_{50.3}Ti_{49.7-x}Hf_x$ ($x \leq 9$ at.%) Shape memory alloys

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ABSTRACT

Transmission electron microscopy and mechanical testing were used to determine the effect of pre-aging (300 °C for 12 h) on microstructure and mechanical behavior of a series of $Ni_{50.3}Ti_{49.7-x}Hf_x$ shape memory alloys ($x = 6$, 8, 8.5, 9 at.%) prior to normal aging at 550 °C for 3.5 h. Pre-aging was found to promote homogenous nucleation of nanosized H-phase precipitates, resulting in improved mechanical stability and strength and 4% recoverable compression strain without permanent deformation. The absence of pre-aging generally resulted in heterogeneous formations of larger H-phase precipitates, primarily clustered along grain boundaries, and correlated with poorer mechanical behavior.

NiTi shape memory alloys (SMAs) have been successfully used in many different fields of engineering because of their functional properties that include shape memory effect (SME) and superelasticity (SE) [1,2]. These properties are due to the occurrence of reversible, thermoelastic martensitic transformations [1–5]. However, work hardening and subsequent aging in the range of 400–550 °C are required to obtain superelastic performances suitable for most applications [2,5–9]. This secondary processing is required because in solid-solution-annealed NiTi, the yield stress is typically less than or equal to the operational transformation stresses. However, the aforementioned aging results in nano-precipitate strengthening via the metastable Ni_4Ti_3 phase [1–8], while cold work imparts dislocation forest structures, the combination of which increase the yield strength of the alloy well above the operational transformation stresses.

Recently, additive manufacturing of NiTi has gained significant attention, as near-net-shaping technology allows for the direct fabrication of complex metallic components [10]. In biomedical applications, the technology provides an ability to print implants to the exact size and geometry optimized for individual patients, revolutionizing their effectiveness [11]. While producing near-net shape components is ideal for manufacturing complex, low production parts, the technology greatly restricts, if not eliminates, the ability to cold work materials after printing. It was well established in the 1980's that precipitation strengthening alone in binary NiTi alloys does not result in high enough yield stresses to promote stable superelastic performance for thousands to millions of cycles [2,5,7,9]. Given the current state of the art in developing shape memory alloys to achieve high strength through precipitation hardening alone, NiTiHf alloys have been identified as some of the best candidates to pursue [12–14].

NiTiHf alloys have primarily been proposed for use in high-temperature aerospace and automotive actuation applications where NiTi cannot perform (>100 °C), as Hf additions elevate the transformation temperatures [13,14]. Hence, most research to date has focused on the shape memory and superelastic behavior of NiTiHf alloys with a high Hf content (15–30 at.%). For these materials, strength and shape memory behaviors are strongly influenced by H-phase nano-precipitates [12–16]. Han et al. first reported the existence of H-phase precipitates in NiTiHf alloys [17], and recently Yang et al. [18] proposed a complete atomic structural model for H-phase.

Aging is an effective way to increase the matrix strength in these alloys by forming fine precipitates that act as pinning sites against the movement of dislocations, while still allowing the martensitic transformation to occur nearly unimpeded. These studies show that in slightly Ni-rich compositions, aging at 550 °C for 3 h is the preferred heat

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treatment to achieve high recoverable strain, high strength, excellent superelastic behavior, and microstructural and dimensional stability due to presence of a homogeneous distribution of densely packed nanosized precipitates throughout the matrix [19–23].

It is already reported that H-phase precipitates are richer in Ni and Hf, their homogeneous distribution in the high (>15 at.%) Hf containing alloys can be attributed to Hf supersaturation in materials that are only slightly Ni-rich, such as the widely studied $Ni_{50.3}(Ti,Hf)_{49.7}$ type alloys. However, alloys with lower Hf content in this stoichiometry range have not been as widely investigated and the effects of heat treatments on H-phase precipitation and resulting properties in these compositions are not currently understood.

This study is part of a larger effort to develop new NiTiHf alloys that can be produced by additive manufacturing for biomedical implants. Consequently, the alloys have to be (mostly) austenitic at body temperature (austenite finish temperature $A_f < 37$ °C in most cases) and thus lower Hf content (6–9 at.%) materials were investigated. In order to strengthen the alloys solely through H-phase precipitation hardening, initially, we tried the same heat treatments found to be close to optimal in the more Hf-rich compositions (Hf > 15 at.%), a single step 550 °C for 3 h aging treatment. However, we found that this treatment did not sufficiently strengthen the alloys. Thus, we looked to recent reports that low temperature thermal cycling combined with room temperature aging leads to Ni clusters that are precursors to the formation of Ni_4Ti_3 precipitates in binary NiTi alloys [24], and hypothesized that analogous low temperature diffusion may result in improved H-phase precipitate morphologies in these moderate Hf-content NiTiHf alloys. In testing the hypothesis, we found that a two-step aging treatment comprised of 1) a low-temperature pre-aging heat treatment, followed by 2) the aging treatment established for higher Hf content alloys, to be effective for these moderate Hf compositions. Hence, we proceeded to investigate the effects and mechanisms of this 2-step treatment on NiTiHf alloys with moderate Hf content.

NiTiHf alloys with target compositions of $Ni_{50.3}Ti_{50-x}Hf_x$, with x = 6, 8, 8.5, and 9 at.% 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 °C for 72 h and then extruded at 900 °C at a 7:1 area reduction ratio. The extruded rods were sectioned into samples that were initially solution-annealed at 1050 °C for 30 min, water quenched, and then pre-aged at 300 °C for 12 h and air-cooled, and finally aged a second time at 550 °C for 3.5 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 °C for 3.5 h after the solution-anneal treatment (without pre-aging at 300 °C for 12 h).

Mechanical compression tests were performed on an MTS servo-hydraulic load-frame equipped with an MTS 661.20 load cell. Compression samples were cylindrical with a diameter of 5 mm and a length of 10 mm. Five compression cycles were applied to the samples using a maximum load of 40 kN and a minimum load of 250 N, corresponding to 2 GPa and 13 MPa engineering stress limits. A cross-head speed of 0.1 mm/min was used, corresponding to an approximate strain rate of 10^{-4} s^{-1} and Ncorr digital image correlation (DIC) software [25] was used to analyze the displacements of the sample. Before each test, eight images of the undeformed sample were acquired and analyzed to establish the strain noise for each pattern, which fell between 10^{-4} to 10^{-5} for the data reported in Fig. 1.

Conventional and high-resolution transmission electron microscopy (HRTEM) 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% HNO_3 in methanol (by volume) at around −35 °C. To measure the size of H-phase precipitates and interparticle distance (the distance of a single precipitate from its closest precipitate), several HRTEM images taken from various regions, were used. This measurement was repeated for almost 100 precipitates on each sample and average precipitate size, average interparticle distance and their corresponding standard error is reported.

Fig. 1 shows the compression responses of the NiTiHf alloys aged at 550 °C for 3.5 h, with (a–d) and without (e–h) an initial pre-aging treatment of 300 °C for 12 h. These tests were performed at room temperature (23 °C), and all the samples were austenitic at the start of the test. They then formed stress-induced martensite upon loading. Depending on the heat treatment, some of the remnant strains when they samples were unloaded can be attributed to martensite that did not transform back to austenite. The amount of strain that was due to retained martensite was phenomenologically assessed by heating the samples to 150 °C and measuring the recovered strains, indicated by the solid arrows in the figure. Strain that was not recovered in this process is phenomenologically attributed to plastic deformation, though we note microscopically, the two mechanisms (retained martensite and plasticity) are usually coupled. Complete recovery of the strain (almost 4%) was observed for all the NiTiHf samples that were pre-aged at 300 °C for 12 h (solid arrows in Fig. 1a–d). For the other samples with 6 to 8.5 at.% Hf (Fig. 1e–f), only a portion of the strain was recovered upon

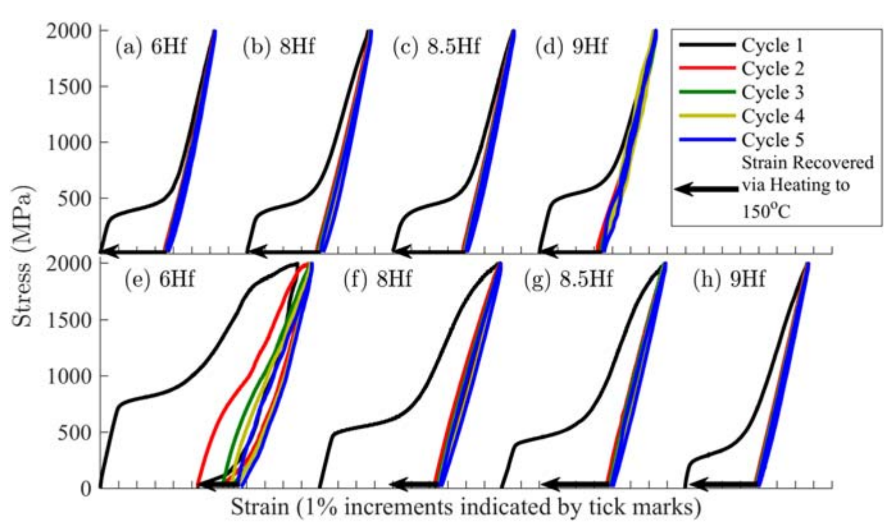

Fig. 1. Mechanical behavior of $Ni_{50.3}Ti_{42.7}Hf_6$, $Ni_{50.3}Ti_{41.7}Hf_8$, $Ni_{50.3}Ti_{41.2}Hf_{8.5}$, and $Ni_{50.3}Ti_{40.7}Hf_9$ (at. %) alloys in compression with (a–d) and without (e–h) the pre-aging treatment at 300 °C for 12 h followed by normal aging at 550 °C for 3.5 h for all samples.