Structure–property relationships in a precipitation strengthened Ni–29.7Ti–20Hf (at%) shape memory alloy

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ABSTRACT

The martensitic transformation temperatures, load-biased thermomechanical properties, and microstructure (characterized by transmission electron microscopy and atom probe tomography) were investigated for a Ni–29.7Ti–20Hf (at%) alloy aged at 550 °C for 0–300 h. Aging for three hours and longer resulted in the precipitation of a face-centered orthorhombic phase, previously denoted as the H-phase. The number density, size, and composition of this phase did not change significantly upon aging from 3 to 30 h. However, continued aging to 300 h resulted in a decrease in the number density and significant coarsening of the precipitates at 550 °C. The alloy exhibited near optimum response for shape memory behavior and dimensional stability after aging for three hours, though transformation temperatures continued to increase with aging time.

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1. Introduction

NiTi alloys, commonly referred to as Nitinol, exhibit a thermoelastic martensitic transformation and consequently are well-known for their shape memory and superelastic properties [1]. Moreover, the transformation temperatures and thus the temperatures at which these various properties occur are highly dependent on composition. With regards to the shape memory effect, considerable interest has been in equiatomic and slightly Ti-rich Nitinol compositions because of their higher transformation temperatures compared to Ni-rich compositions. Tang [2] has summarized the work of many groups concluding that small increases in Ni content for compositions above 50 at% resulted in a precipitous drop in the transformation temperatures to well below room temperature. However, unlike the equiatomic and Ti-rich compositions, which generate significant residual strains during thermomechanical cycling through the transformation regime [1,3,4], the Ni-rich compositions exhibit excellent dimensional stability during pseudoelastic stress cycling and load-biased thermal cycling because of precipitation strengthening effects [5–7]. Dimensional stability refers to the material maintaining a fixed dimensional tolerance during multiple transformation cycles, an attribute critical in actuator based applications. The ability to

increase the transformation temperatures through ternary additions, while retaining the excellent dimensional stability observed in Ni-rich compositions, has been an active goal in shape memory alloy (SMA) research in recent years [8,9].

Several of the earlier efforts focused on the use of precious metal additions for increasing transformation temperatures combined with overall compositions that were basically Ti-lean in stoichiometry in an effort to generate precipitate strengthened SMA with greater stability. Kovarik et al. [10] reported the formation of a monoclinic precipitate phase, denoted as the P-phase, in a Ni–Ti–Pt alloy. Subsequent to this report, Sasaki et al. [11] reported the same phase in a Ni–Ti–Pd SMA. In both systems, the precipitate was Ni-rich relative to the matrix and formed coherent/semi-coherent interfaces, which provided the necessary compositional alterations and strain that raised the transformation temperatures above 100 °C [12]. Unfortunately, these types of precious metal additions are cost-prohibitive for developing alloys for wide-spread bulk applications.

A similar strategy has been used quite successfully to develop precipitate strengthened Ni–Ti–Hf [13–15] and Ni–Ti–Zr [16,17] high-temperature SMAs with good work output, stable large-strain pseudoelastic behavior at elevated temperatures, and nearly unprecedented dimensional stability during thermomechanical cycling. The Hf and Zr macro-additions provide a much lower cost alternative relative to the precious metal containing alloys. As with the prior systems, an increase in the transformation temperatures, over solution treated conditions, was associated with the

precipitation of nanoscale phases that affected the bulk composition and strain within the matrix. These precipitates, denoted as the H-phase, were confirmed as a face-centered orthorhombic structure in various Ni-rich compositions of Ni–Ti–Hf and Ni–Ti–Zr alloys [18,19], consistent with the phase that was first reported by Han et al. [20].

In this paper, we investigate the structure–property relationships in greater detail for a Ni–29.7Ti–20Hf (at%) alloy that undergoes H-phase precipitation. Using transmission electron microscopy (TEM) and atom probe tomography (APT), the precipitate structures formed at 550 °C for various aging times were characterized and correlated to the transformation temperatures, the stability of the transformation temperatures with repeated thermal cycling, and the load-biased shape memory behavior of the alloy. This information provides necessary insights on the optimization of the H-phase precipitation with respect to shape memory properties of the alloy.

2. Experimental procedure

A 600 g ingot of nominal composition Ni–29.7Ti–20Hf (at%) was vacuum induction melted using relatively high purity elements (99.98 Ni, 99.95 Ti. 99.9 Hf)) in a graphite crucible under a partial pressure of argon. The melt was cast into a cylindrical copper chill mold (25.4 mm diameter $\times \sim 102$ mm long) with a built-in conical hot-top to accommodate shrinkage during solidification. The resulting ingot was vacuum homogenized for 72 h at 1050 °C and furnace cooled and subsequently sealed in a mild steel can (after removing the hot top) for extrusion. The nominally 25.5 mm diameter ingot was then extruded into a rod with approximately 10 mm diameter in a single pass at 900 °C. The extrusion can was removed by grinding and the as-extruded SMA was then sectioned, solution annealed at 1050 °C for 3 h, and immediately water quenched followed by aging treatments at 550 °C for varying times up to 300 h and again water quenched. All solution annealing and aging treatments were conducted in a tube furnace under a continuous flow of ultra-high purity Ar with the specimens wrapped in Ta foil to reduce oxidation of the specimens.

Hardness testing was conducted on a Buehler Model 1600-6100 microhardness tester equipped with a Vickers diamond-pyramid indenter using a load of 500 g. Each specimen was indented 10 times from which the mean hardness and standard deviation were determined and the values plotted as an age hardening curve.

Differential scanning calorimetry (DSC) was performed using a TA Instrument DSC Q1000 with heating and cooling rates of 10 °C/min to determine the stress-free phase transformation temperatures. Austenite-start (A_s) and austenite-finish (A_f) temperatures on heating and the martensite-start (M_s) and martensite-finish (M_f) temperatures on cooling were determined by the baseline tangent method. At least four heating and cooling cycles were performed with the DSC instrument to determine the stability of the phase transformation temperatures for each condition.

The thermo-mechanical response of the alloy was determined using an MTS 810 servo-hydraulic load frame managed with an MTS FlexTest SE digital controller. Cylindrical samples, 5 mm diameter by 10 mm in length, were compressed between Udimet-720 platens, which were backed by hot grip extension rods held by water-cooled MTS 646 hydraulic collet grips. Load was measured with a 100 kN load cell. Strain in the sample was measured with a high resolution Micro-Epsilon OptoControl 2600 LED extensometer. Heating of the sample was performed using a Eurotherm temperature controller coupled with an Ameritherm Novastar 7.5 kW induction heater, which directly heated the hot grip extension rods. The platens and sample were then heated via thermal conduction through the hot grips. The specimen temperature was measured by a type-K thermocouple spot-welded directly to the middle of the specimen gage.

During the load-biased thermal cycling experiments, the "no load" condition actually corresponded to tests with -1 to -3 MPa applied stress, which was the minimum applied force needed to maintain contact between the specimen and platens. This condition is labeled as "0 MPa" in the presentation of the data. Mechanical loading beyond the no load condition was controlled at a strain rate of 1×10^{-4} s^{-1} until the desired applied stress was reached at room temperature. The system was then switched to load-control followed by thermal cycling under a constant applied load. Specimens were tested at -50 MPa, and then in -100 MPa increments from -100 MPa to -700 MPa. At each stress level, temperature was cycled between 40 °C and 300 °C at a rate of 20 °C/min or slower where the inherent convection of the material in room temperature air limited the temperature rate (i.e., upon cooling near ambient temperature). Two thermal cycles were carried out at each stress level; the second of these cycles is reported in the presentation of the data.

The microstructure after various aging conditions was characterized by TEM and APT. With regards to TEM specimen preparation, a 3 mm disc was cut from the heat-treated sample, ground to ~ 100 μm in thickness using SiC papers, and then dimpled to a final thickness of < 15 μm using a 6 μm diamond suspension in a Fischione Model 200 Grinder. Once dimpled, the discs were then ion milled using a Gatan Model 691 Precision Ion Polishing System until electron transparent perforations formed in the dimpled region. The TEM analysis was performed using a FEI Tecnai G^2 F-20 Supertwin (scanning) transmission electron microscope ((S)TEM) operated at 200 keV.

APT was performed using a Cameca Local Electrode Atom Probe (LEAP) 3000XSi. The atom probe specimens were lifted-out from the bulk sample and placed onto pre-fabricated Si posts using a FEI Quanta 200 3D Dual Beam scanning electron-focused ion beam microscope equipped with an Omniprobe micromanipulation lift-out system. Once attached to the Si post, the specimens were annular milled to yield the appropriate geometric needle shape with a radius of ~ 100 nm required for field evaporation. The details of the FIB-based atom probe preparation can be found elsewhere [21,22]. The specimens were maintained at a base temperature of 30 K (-243 °C) and thermally assisted field evaporated using a laser mode at a pulse rate of 200 kHz, pulse energy 0.2 nJ, and a target evaporation set at 0.5. The atom probe data was reconstructed using the IVAS 3.6.6 software package.

3. Results and discussion

Fig. 1(a) shows the evolution of Vickers hardness as a function of aging time. The lowest hardness value of 353 ± 8 VHN was recorded for the solution annealed condition and a slight increase to 371 ± 9 VHN was noted after aging for 0.1 h. The hardness peaked at 492 ± 8 VHN after 100 h aging and decreased to 481 ± 3 VHN after 300 h.

Fig. 1(b) shows the DSC curves containing four thermal cycles for each specimen for various heat-treated conditions. All the DSC curves show a set of endothermic peaks corresponding to the martensite-to-austenite transformation upon heating and exothermic peaks for the austenite-to-martensite transformation upon cooling. The start and finish temperatures of the martensite and austenite phase transformations are listed in Table 1 for the second thermal cycle of each condition shown in Fig. 1(b) (solution annealed, 0.3 h, 3 h, 30 h and 300 h), which are the focus of the microstructural studies presented below.

Interestingly, the specimen with the 0.3 h heat treatment exhibited a decrease in transformation temperatures compared to the solution annealed material. A similar decrease in transformation temperatures for early aging times and low aging temperatures has