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Transformation strains and temperatures of a nickel–titanium–hafnium high temperature shape memory alloy

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Abstract

A combined experimental and theoretical investigation of the transformation temperature and transformation strain behaviors of a promising new $Ni_{50.3}Ti_{29.7}Hf_{20}$ high-temperature shape memory alloy was conducted. Actuation behavior of single crystals with loading orientations near $[0\,0\,1]_{B2}$, $[\bar{1}\,1\,0]_{B2}$, and $[1\,1\,1]_{B2}$, as well as polycrystalline material in aged and unaged conditions was studied, together with the superelastic, polycrystalline torsion response. These results were compared to analytic calculations of the ideal transformation strains for tension, compression, and torsion loading of single crystals as a function of single crystal orientation, and polycrystalline material of common processing textures. H-phase precipitates on the order of 10–30 nm were shown to increase transformation temperatures and also to narrow thermal hysteresis, compared to unaged material. The mechanical effects of increased residual stresses and numbers of transformation nucleation sites caused by the precipitates provide a plausible explanation for the observed transformation temperature trends. Grain boundaries were shown to have similar effects on transformation temperatures. The work output and recoverable strain exhibited by the alloy were shown to approach maximums at stresses of 500–800 MPa, suggesting these to be optimal working loads with respect to single cycle performance. The potential for transformation strain in single crystals of this material was calculated to be superior to binary NiTi in tension, compression, and torsion loading modes. However, the large volume fraction of precipitate phase, in part, prevents the material from realizing its full single crystal transformation strain potential in return for outstanding functional stability by inhibiting plastic strain accumulation during transformation. Finally, calculations showed that of the studied polycrystalline textures, $[0\,0\,1]_{B2}$ fiber texture results in superior torsion performance, while $[0\,1\,1]_{B2}$ fiber texture results in superior tensile behavior, and both $[0\,1\,1]_{B2}$ and random textures will result in the best possible compression performance.

Keywords: Orientation; Texture; Precipitates; Grain boundaries; Transformation strain

1. Introduction

Substituting hafnium (Hf) or zirconium (Zr) for titanium (Ti) in near equiatomic compositions of nickel–titanium (NiTi) results in shape memory alloy (SMA) systems that have the ability to realize high transformation

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temperatures (up to 400 °C) [1,2] relative to binary NiTi (up to ∼100 °C) [3]. Additionally, aging of slightly Ni-rich NiTi(Hf,Zr) compositions may result in precipitate structures that provide additional strength to the alloys and stabilize microstructure evolution, such that there is no need for additional cold work or thermo-mechanical processing to achieve stable, repeatable actuation and superelastic performances [4–12]. In studying the effect of heat treatments between 400 °C and 650 °C on $Ni_{50.3}Ti_{29.7}Hf_{20}$, a 550 °C, three-hour aging has been shown to result in optimized strength, exhibiting a macroscopic austenite yield stress of at least 1300 MPa [7], and minimized thermal hysteresis of ∼25 °C [13]. These enhanced properties relative to the unaged alloy are attributed to a high density of very fine and evenly dispersed orthorhombic "H-phase" precipitates on the order of 10–25 nm long, 5–10 nm wide [12–15]. These precipitates have been shown to be coherent with the B2 austenite matrix, semi-coherent with the B19' martensite [12,15]. The transformation temperatures of this aged alloy under moderate operating stresses range between 120 °C and 200 °C, [4,6,13] making it a suitable candidate for applications requiring higher transformation temperatures than those that are achievable in binary NiTi. With the initial process–structure–property characterization indicating that this alloy has potential to enable applications that are not feasible with binary NiTi, further efforts to characterize this alloy are underway with a focus on performance issues such as fatigue life and material behavior in engineering components [16].

One issue central to the optimization of SMA performance is that of texture [17–20]. Because of the low symmetry of the B19' structure, the martensite phase inherently exhibits diverse orientation-specific properties [20–26]. Furthermore, during phase transformation, the ability of the B2 austenite structure to transform to any of twelve B19' variants, together with the non-centrosymmetry of the B19' structure, results in asymmetric transformation and reorientation behaviors. Together, these phenomena manifest in transformation and martensite deformation asymmetries with respect to loading mode (i.e., tension, compression, shear), even of random polycrystals [17–20,26–33]. Imparting texture to a polycrystal results in anisotropic macroscopic responses in addition to this asymmetry [17–20,34–36]. Thus, the desired processing texture for an application using an SMA torque tube need not be the same as the optimal texture for a wire in tension or a helical spring in compression.

Toward elucidating the orientation–texture-performance relationships of aged $Ni_{50.3}Ti_{29.7}Hf_{20}$ SMA, we provide a combined experimental–numerical study on the recoverable strains and transformation temperatures of single crystals of unique orientations and polycrystals of near random texture. More specifically, we use analytic calculations to bound the maximum possible transformation strains of single crystals of the alloy, and we also bound the maximum and minimum recoverable strains to be expected of polycrystals of several common textures subjected to tension, compression, and torsion loads. We then compare experimental data with these bounds and draw insights into the nuances of the physics of the real materials and also how they lead to deviations from theoretical limits on transformation strains.

2. Methods

2.1. Material processing

$Ni_{50.3}Ti_{29.7}Hf_{20}$ ingots were vacuum induction melted in graphite crucibles under a protective argon atmosphere using high purity elemental constituents (99.995 wt.% Ni, 99.7 Hf, 99.995 Ti) and cast into a 25.4 mm diameter by 102 mm long copper mold. The mold was designed with a conical hot-top section to accommodate shrinkage within the casting during solidification. The resulting ingots were vacuum homogenized for 72 h at 1050 °C and furnace cooled. After homogenization, the ingots were processed in one of two ways – polycrystal extrusion or single crystal growth. For extrusion, the hot tops were removed, the ingots sealed in mild steel cans, and extruded at 900 °C through an area reduction of 7:1. For single crystal growth, ingots were used as pre-alloyed melt stock for single crystal processing using a graphite crucible under an inert helium gas atmosphere via an advanced Bridgman technique to produce approximately 30 mm diameter single crystals. The material used for the axial–torsion samples was cast using a cold-crucible vacuum induction melting process, but were otherwise processed identical to the polycrystalline material described above [37].

Two different sample geometries were generated from the polycrystal extrusions; 5 mm diameter by 10 mm long compression cylinders and axial–torsion thin-walled tubes with 3.5 mm inside diameter, 4.5 mm outside diameter by 17.8 mm long gage sections. They were fabricated using a combination of wire electrical discharge machining (EDM), centerless grinding, and turning operations. The as-grown single crystals were oriented using Laue diffraction and samples were cut via wire EDM into 4 mm × 4 mm × 8 mm parallelepipeds in three orientations: $[0\,0\,1]\{3\,4\,0\}_{B2}$, $[\bar{3}\,4\,0]\{4\,3\,0\}_{B2}$, and $[6\,7\,8]\{4\,3\,0\}_{B2}$. High temperature (such that the alloy was fully austenitic) Laue diffraction determined the orientation of the $[0\,0\,1]_{B2}$ single crystal to have a misalignment of $1.7° \pm 0.3°$. Regarding the latter orientations: $[\bar{3}\,4\,0]_{B2}$ is 90° from the $[0\,0\,1]_{B2}$ and 8.13° from the $[\bar{1}\,1\,0]_{B2}$, which is equivalent through symmetry to the $[0\,1\,1]_{B2}$; the $[6\,7\,8]_{B2}$ is 49.05° from the $[0\,0\,1]_{B2}$ and 6.65° from the $[1\,1\,1]_{B2}$. Thus, the three orientations are or are close to $[0\,0\,1]_{B2}$, $[\bar{1}\,1\,0]_{B2}$ or $[0\,1\,1]_{B2}$, and $[1\,1\,1]_{B2}$.

All single crystal samples were studied in the as-grown condition, with no additional thermal or mechanical treatments. However, the thermal conditions encountered during Bridgman processing resulted in precipitation and growth of the H-phase precipitates (see Section 3.1),