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Nanoindentation studies of small-scale martensitic transformations and ductile precipitate effects in dual-phase polycrystalline shape memory alloys

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Abstract—A ductile solid solution phase γ is introduced into austenite β of a polycrystalline Co–Ni–Al Shape Memory Alloy (SMA) using thermal treatments. Thermally-induced martensitic transformation in this dual-phase SMA is detected by Differential Scanning Calorimetry and X-ray Diffraction. We perform nanoindentation tests using a Berkovich tip to study mechanically-induced martensitic transformations and transformation–precipitate interactions. Deviation of load–depth curve of austenite β from Hertz elastic prediction indicates initiation of plastic deformation and possibly also martensitic transformation, the occurrence of which is supported by stress analysis. Compared to non-transforming γ, strain recovery is significantly higher and percent energy dissipation is much lower in β. Indents in β but at β/γ interfaces exhibited enhanced strain recovery, higher nanohardness, and lower energy dissipation in comparison to austenite β. There is local strengthening at the β/γ interface. Additionally, γ accommodates transformation strain in nearby β by extensive plastic deformation, alleviating stress concentration beneath the indenter. The plastic accommodation by γ also relieves the constraint imposed on transforming β and decreases the energy barrier for transformation. As a result, less material deforms plastically and more transforms martensitically, improving superelastic properties in β adjacent to γ. Our results suggest that incorporation of a ductile second phase is promising for enhancing ductility and superelasticity of polycrystalline SMAs.

Keywords: Dual-phase Shape Memory Alloys (SMAs); Martensitic transformation; Nanoindentation; Ductile precipitate effects; Superelasticity

1. Introduction

Shape Memory Alloys (SMAs) hold a great promise for actuation, sensing, and damping applications [1]. They can sustain large strains when a force is applied, and recover their prior shape and dimensions upon release of the force or application of heat. The shape memory effect is enabled by a reversible martensitic phase transformation, through which austenite and martensite phases with different crystal structures convert between each other mainly by a shear [2]. During thermally-induced transformation, martensite variants self-accommodate to minimize strain energy; but under an applied stress one or a few variants are promoted over others and the self-accommodated configuration no longer exists, leading to macroscopic strain. Many single crystalline SMAs have been studied (e.g. Ni–Ti [3–5], Ni–Mn–Ga [6], Cu-Al–Ni [7], Cu–Zn–Al [8,9], and Co–Ni–Ga [10]) and some can achieve recoverable strains up to 10% in tension [11]. In polycrystalline SMAs, however, during stress-induced transformation different grains may shear in different directions, which often induces strain incompatibility and stress concentration at grain boundaries, leading to intergranular fracture. For example, while single crystalline [12,13] and oligocrystalline [14–16] Cu–Al–Ni exhibits high recoverable strains, its bulk polycrystalline forms are prone to grain boundary cracking [17,18]. On the other hand, polycrystalline Ni–Ti SMAs exhibit excellent transformation ductility (possibly due to their particular transformation crystallography and grain texture [19]), but are expensive and have only moderate fatigue properties [20]. It is therefore desirable to develop polycrystalline SMA alternatives that are not only ductile but low cost. Dual-phase design of polycrystalline SMAs is a scientifically intriguing concept with promising technological potential.

Dual-phase concept has been explored in many SMA systems. Some SMA systems can precipitate an intermetallic second phase, such as Ti_2Ni or Ti_3Ni_4 in Ni–Ti [21,22], H-phase in Ni–Ti–Hf(Zr) [23–25], γ′ in Co–Ni–Ga [26,27], and γ in Cu–Zn–Al [28–36]. Ti_2Ni and Ti_3Ni_4 precipitates increase hardness and enhance superelastic properties in Ni–Ti [21,22]. H–phase precipitates smaller than 100 nm in Ni–Ti–Hf(Zr) strengthen the matrix and improve shape memory properties of polycrystals, which achieve full shape recovery (∼3%) at 180–250 °C [23,24]. 10–25 nm γ′ precipitates in Co–Ni–Ga single crystals are effective at strengthening austenite and resisting plastic deformation [26], leading to complete recovery of nearly 3% compressive strain up to 300 °C [27]. Oriented γ′ precipitates result in higher transformation temperatures and smaller hysteresis than do non-oriented ones due to the ease of martensite

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accommodation around oriented γ′ precipitates [27]. In Cu–Zn–Al single crystals, while larger γ precipitates (∼500 nm) tend to increase martensitic transformation temperature and narrow hysteresis with thermal cycling, smaller ones (∼15 nm) facilitate the stabilization of transformation during cycling [28]. As these intermetallic second phases discussed above were studied in either Ni–Ti based SMAs or single crystals of Cu–Zn–Al or Co–Ni–Ga, they do not provide a solution for the long-standing transformation brittleness issue in many polycrystalline SMAs such as Ni–Mn–Ga, Cu–Al–Ni, Cu–Zn–Al, Co–Ni–Ga, or Co–Ni–Al.

Several SMA systems that exhibit brittleness associated with grain boundaries in polycrystalline austenite β phase can precipitate a non-transforming and ductile solid solution phase γ. Studies on Ni–Al [37], Co–Ni–Al [38–40], Co–Ni–Ga [41], Ni–Al–Fe [42], and Ni–Mn–Ga [43] have reported enhancement of ductility of β polycrystals when the γ phase was precipitated into them. For example, Ni–Al alloys exhibit β/γ equilibrium when alloyed with Co, Cr, Fe, Mn, or Cu; additions of these elements to polycrystalline Ni–Al SMAs, which are extremely brittle, drastically improve room-temperature and elevated-temperature ductility and workability due to the formation of a ductile γ phase [37]. γ may preferentially precipitate along grain boundaries, cushioning grain boundaries as they are stressed [37,44]. The presence of γ alters the fracture mode from intergranular cracking in single β phase Ni–Al to transgranular with ductile tearing in (Co, Cr, Fe, Cu)–Ni–Al dual-phase alloys [37]. In β + γ dual-phase Co–Ni–Al polycrystals, as the volume fraction of γ increases from 18% to 40%, the strain to failure increases significantly from 19% to 40%, and cold workability also improves [45]. Polycrystalline Ni–Mn–Ga and Ni–Mn–Fe–Ga also show an increase in plasticity with additions of γ phase [43].

Interestingly, the addition of a non-transforming phase does not seem to compromise superelastic strain and recovery. For example, [1 1 5] oriented Co–Ni–Al single crystals with a β + γ microstructure achieve a recoverable strain of 5.5–6% in tension [11,46] and 3.3% in compression [46]. [0 0 1] and [1 2 3] oriented Co–Ni–Al crystals with a β + γ dual-phase microstructure achieve 4.1% and 3.3% compressive superelastic strains [46], while those for their β phase counterparts are 4% and 2.5%, respectively [47]. A dual-phase Co–Ni–Al polycrystalline alloy containing γ achieves a recoverable strain of 4% following five cycles in compression [48]. A Co–Ni–Ga polycrystal containing β and γ have a compressive shape memory strain of 5.1% [41], while Co–Ni–Ga β phase single crystals (oriented along [0 0 1], [0 1 1], and [$\bar{1}$ 2 3]) have recoverable transformation strains of 4.5%, 4.0%, and 3.5% in compression, respectively [49].

Despite the above studies on dual-phase SMAs, the direct localized effect of a ductile second-phase on superelastic properties is presently unclear. The key to develop and optimize dual-phase SMAs lies in understanding martensitic transformation–precipitate interactions at austenite/precipitate phase boundaries. Instrumented nanoindentation is suited for gaining such understanding. Nanoindentation has been used to probe the localized mechanical properties of SMA thin films [50–52], single crystals [53], bulk polycrystals [54,55], and nanopillars [56], and has been shown to be able to detect superelastic behavior [51,52]. Some studies utilized a cono-spherical or spherical indenter tip with a large nominal radius (e.g. 0.6 μm [56], 1 μm [57], 2 μm [52], 5 μm [58], 10 μm and 650 μm [59]) for nanoindentation on SMAs to reduce stress concentration and plasticity beneath the tip, and accordingly used high indentation loads, on the order of tens of mN [54,58,60]. Others used a Berkovich tip of 50–200 nm nominal radius [50,53–55,57,59,61,62] that probes smaller volumes. One study used a Berkovich tip and applied cyclic loads with a peak value of 1000 μN to Ni–Ti thin films, and demonstrated stabilization of superelasticity after 6 cycles [50]. Nanoindentation has also been used to probe the local effects of small precipitates on mechanical properties in dual-phase alloys (non-SMAs). For example, it has been applied to a γ/γ′ nickel-based superalloy to measure the hardness of γ with a 250 nm channel width and γ′ precipitates of 100–790 nm size [63]. It was also used to measure hardness and modulus of γ′ precipitates smaller than 100 nm in CMSX-6 and Waspaloy superalloys [64]. Nanoindentation has also been used to measure local hardness [65] and probe plastic zone–grain boundary interactions in dual-phase steel consisting of martensite grains smaller than 4 μm and ferrite grains smaller than 1.5 μm [66].

Our main goal is to study the superelastic properties of dual-phase SMAs at small scales using nanoindentation, and elucidate martensitic transformation–ductile precipitate interactions across phase boundaries. We also study grain orientation effect on small-scale martensitic transformations. In this study, we use a Co–Ni–Al SMA as a model material and study the effects of a ductile solid solution phase γ. Co–Ni–Al has excellent corrosion resistance, very high yield strength (∼0.6–1.2 GPa [37,67,68]), and high melting temperature, making it a desirable low-cost candidate material for both ambient and high temperature applications [69]. Its high yield stress also helps suppress yielding during low-load nanoindentation and facilitates our study of martensitic transformations. The understanding and insights gained from this study will be applicable or adaptable to many other dual-phase SMA systems.

2. Experimental procedure

Cylindrical ingots of $Co_{37}Ni_{35.5}Al_{27.5}$ at.% were prepared by arc melting and casting in a copper chill mold in high purity argon. The as-prepared polycrystalline alloy was subjected to a thermal treatment in argon with 1% hydrogen at 1150 °C for 24 h [70]. Fig. 1(a) illustrates our alloy composition (as a red dot), which is located in the β + γ dual-phase regime in an isothermal Co–Ni–Al ternary phase diagram. From an analysis of the phase diagram and the use of reported tie lines [69], it is expected that approximately 18–20 wt.% γ exists in equilibrium with β as a result of this thermal processing. Fig. 1(b–d) shows the unit cells of austenite β, martensite β′, and γ in Co–Ni–Al. The austenite β phase, which has a B2 crystal structure, transforms to tetragonal $L1_0$ martensite (by shrinking along the “a” axes while expanding along “c”). γ phase is a face-centered cubic solid solution consisting of Co, Ni, or Al atoms at each lattice site [69].

A Differential Scanning Calorimeter (TA instruments DSC-Q2000) was used to measure martensitic transformation temperatures with a temperature ramping rate of 2 °C/min. Transformations were further confirmed by in-situ X-ray Diffraction (XRD). XRD patterns were collected with Cu–Kα radiation using a Bruker D8-Discover Diffractometer equipped with a thermally controlled stage capable of reaching temperatures in the range of −100 °C