Scripta Materialia 115 (2016) 113–117

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

# Grain boundary engineering of Co–Ni–Al, Cu–Zn–Al, and Cu–Al–Ni shape memory alloys by intergranular precipitation of a ductile solid solution phase

Rebecca D. Dar, Haoxue Yan, Ying Chen *

*Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180, USA*

ARTICLE INFO

*Article history:*
Received 12 November 2015
Received in revised form 5 January 2016
Accepted 8 January 2016
Available online 25 January 2016

*Keywords:*
Shape Memory Alloys (SMA)
Grain Boundary Engineering
Precipitation
Ductility
Martensitic phase transformation

ABSTRACT

Many polycrystalline shape memory alloys, e.g., Co–Ni–Al, Cu–Zn–Al, and Cu–Al–Ni, undergo intergranular fracture. To improve their transformation ductility, we perform Grain Boundary Engineering and stimulate the precipitation of a ductile second phase, which is a face-centered-cubic solid solution, along grain boundaries, by tailoring composition and thermal processing. Orientation imaging confirms precipitation along grain boundaries and unimpeded martensite growth toward grain boundary precipitates. Differential Scanning Calorimetry confirms reversible martensitic transformations in these dual-phase samples. These precipitates can accommodate transformation strain, relieve constraint in adjacent austenite grains, and arrest cracks by extensive plastic deformation, thereby improving transformation ductility and shape memory effects.



Shape Memory Alloys (SMAs), due to their ability to undergo reversible martensitic transformations and recover large strains, are promising for many applications such as actuation [1,2], energy conversion [3,4], damping [1,5], and sensing [6,7]. Ni–Ti SMAs are known for their excellent shape memory properties and transformation ductility even in polycrystalline forms (possibly due to their particular transformation crystallography and grain texture [8]), but they are relatively expensive and have only moderate fatigue properties [9]. Many other SMAs, such as Cu–Zn–Al [10,11], Cu–Al–Ni [12], Co–Ni–Al [13–15], Co–Ni–Ga [16], and Ni–Mn–Ga [17], have excellent shape memory properties when they are single crystalline. However, they are typically brittle and prone to intergranular fracture in polycrystalline forms. The transformation shear occurs in different directions in different grains during stress-induced martensitic transformation, resulting in stress concentration at grain boundaries and subsequently fracture along them.

Efforts have been attempted for improving the ductility of these polycrystalline SMAs and typically involve manipulating the grain size. For example, grain refinement, achieved by adding elements such as Zr, Ti, B, V, Cr [18], Gd [19], has been utilized in polycrystalline SMAs such as Ni–Mn–Ga [19], Cu–Zn–Al [18,20], Cu–Al–Ni [21], and Cu–Al–Ni–Ti [22], as finer grains provide better strain accommodation (for example, they alter the fracture mode from intergranular to mostly ductile transgranular during fracture impact test [18,21]). On the other hand, excellent shape memory and transformation ductility have been achieved in oligocrystalline SMAs such as bamboo-grain-structured microwires [23–25], where triple junctions are eliminated, grain boundary area is minimized, and surface relaxation is significant, reducing strain incompatibility at grain boundaries [26]. However, for both oligocrystalline and bulk polycrystalline SMAs, it is still highly desirable and in many cases necessary to increase the resistance to fracture in grain boundary regions during stress-induced transformations for practical use.

In this paper, we demonstrate a Grain Boundary Engineering (GBE) approach for several typical brittle polycrystalline SMAs, including Co–Ni–Al, Cu–Zn–Al, and Cu–Al–Ni systems, which have different crystallographic transformation pathways and thermomechanical properties. Moreover, Co–Ni–Al and Cu–Al–Ni are promising inexpensive candidates for high temperature SMAs. In the phase diagrams for these and many other SMA systems (see Fig. 2), the austenite regime is bordered by a dual-phase regime comprised of austenite and a solid solution phase with a Face-Centered-Cubic (FCC) crystal structure. The present GBE approach involves precipitation of a thin layer of the non-transforming, ductile FCC solid solution phase along grain boundaries in the austenite phase, as illustrated in Fig. 1(b). Compared to GBE methods that involve thermomechanical processing [27], the present *grain boundary phase engineering* approach is straightforward to implement and is scalable at a low cost. It is applicable to bulk polycrystals as well as wires, ribbons and sheets, and porous SMAs.

The addition of an FCC solid solution second phase to extremely brittle single-phase polycrystalline SMAs has been found to significantly improve ductility [28–32]. This is evident in Fig. 1(e) and (f), which

* Corresponding author.
*E-mail address:* cheny20@rpi.edu (Y. Chen).

http://dx.doi.org/10.1016/j.scriptamat.2016.01.014

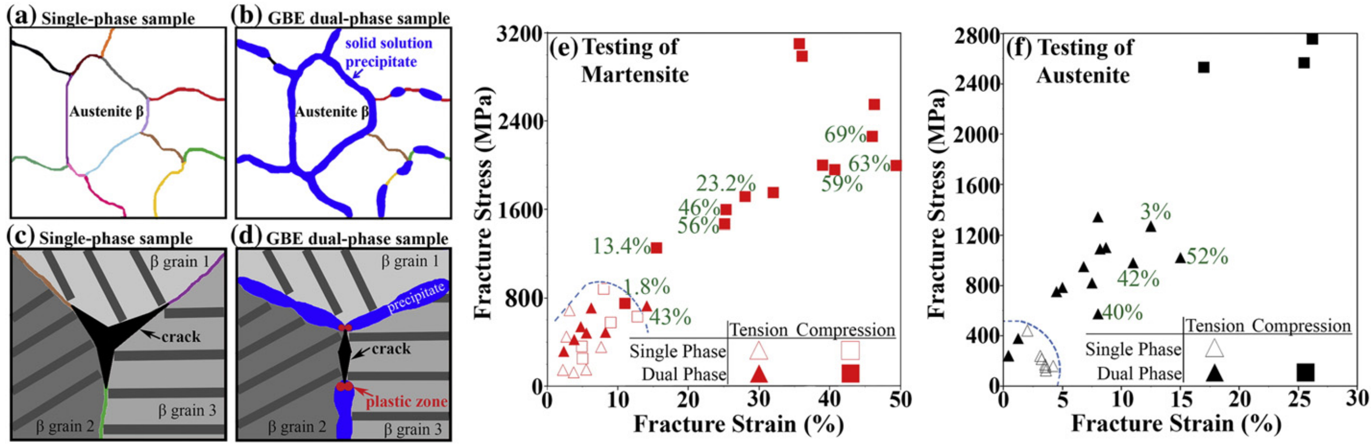


**Fig. 1.** (Color online) Schematic comparisons between single-phase SMAs (a, c) and grain boundary engineered (GBE) dual-phase samples where a thin layer of an FCC solid solution phase (in blue) precipitates along grain boundaries (b, d). During formation of martensite (in dark gray), cracks may propagate along grain boundaries in single-phase samples (c), but may be arrested by ductile precipitates at grain boundaries (d). Literature results for polycrystalline SMAs initially in martensitic and austenitic state are assembled in (e) and (f), respectively. Single phase data (open symbols) are enclosed by dashed blue lines, and include Cu–Al [54], Cu–Al–Ni [33,54–56], Cu–Al–Ni–Ti–Cr [54], Cu–Al–Be–B [57], Co–Ni–Ga [51], and Ni–Mn–Ga [31]. Non-GBE dual-phase data (filled symbols) include Co–Ni–Al [28,32,58], Co–Ni–Ga [51], Ni–Al–Fe [28,35], Ni–Al–Cr [28], Ni–Mn–Ga and Ni–Mn–Fe–Ga [31], Ni–Mn–Cu–Ga [59], Ni–Mn–Co–Ga [60], Ni–Mn–Fe–In [61], and Fe–Mn–Al–Ni [29]. The FCC solid-solution second-phase fraction, if known, is also provided.

summarize literature data for fracture stress and fracture strain of polycrystalline SMAs initially in martensitic and austenitic state, respectively. In Fig. 1(e–f), data for dual-phase SMAs containing an FCC solid solution phase are shown as filled symbols; there is some spread in data due to different alloys and compositions, testing temperatures (mostly at room temperature) with respect to transformation temperatures, and second phase fractions. When the matrix is initially martensitic, martensite variant reorientation and conversion occurs at low loads [33,34] while at high loads dislocation plasticity might take place [34]. In Fig. 1(e), the fracture strain for single-phase samples was mostly below 10%, but was as high as 50% in dual-phase samples. However, testing SMAs that are initially austenitic and undergo martensitic transformation upon loading beyond a critical stress is more relevant to applications. In most brittle single-phase polycrystalline samples, fracture occurs before the transformation is complete. In Fig. 1(f), the majority of single-phase data is clustered around 2.5–4.5% fracture strain while dual-phase values are mostly 5–30%. However, in these prior studies, the materials are non-GBE dual-phase SMAs, i.e., the precipitation was not intentionally controlled along grain boundaries and a high fraction of precipitates were present throughout the grains. While grain interior precipitates significantly improve alloy ductility, they replace transforming material and may interfere with reversible transformation, reducing the overall recoverable strain and impeding strain recovery. In GBE dual-phase samples as illustrated in Fig. 1(b), however, precipitation of the second phase occurs primarily along grain boundaries. This has an optimal effect on ductility because the second phase can cushion grain boundaries, which are the weak links, as they are stressed [28,35]; the formation of a network of thin intergranular precipitates requires a very small volume fraction of precipitates compared to non-GBE dual-phase materials, minimizing the effect on martensitic transformation inside grains. We tailor alloy composition and thermal treatment sequence, temperature, and duration to promote grain boundary precipitation and control the fraction and morphology of the precipitates in Co–Ni–Al, Cu–Zn–Al, and Cu–Al–Ni polycrystalline SMAs [36].

Cast ingots of $Co_{45.46}Ni_{39.40}Al_{15.14}$ wt.% and $Cu_{70}Zn_{26}Al_4$ wt.% were prepared by arc melting and casting in a copper chill mold in high purity argon and $Cu_{86}Al_{11}Ni_3$ wt.% was purchased from American Elements. These alloy compositions are marked as a red dot in Fig. 2(b), (d), and (f), respectively; they all lie inside the austenite plus solid solution dual-phase regime in each of these isothermal phase diagrams. Thermal treatments were carried out in argon with 1% hydrogen, at relatively high temperatures within the temperature range where two-phase

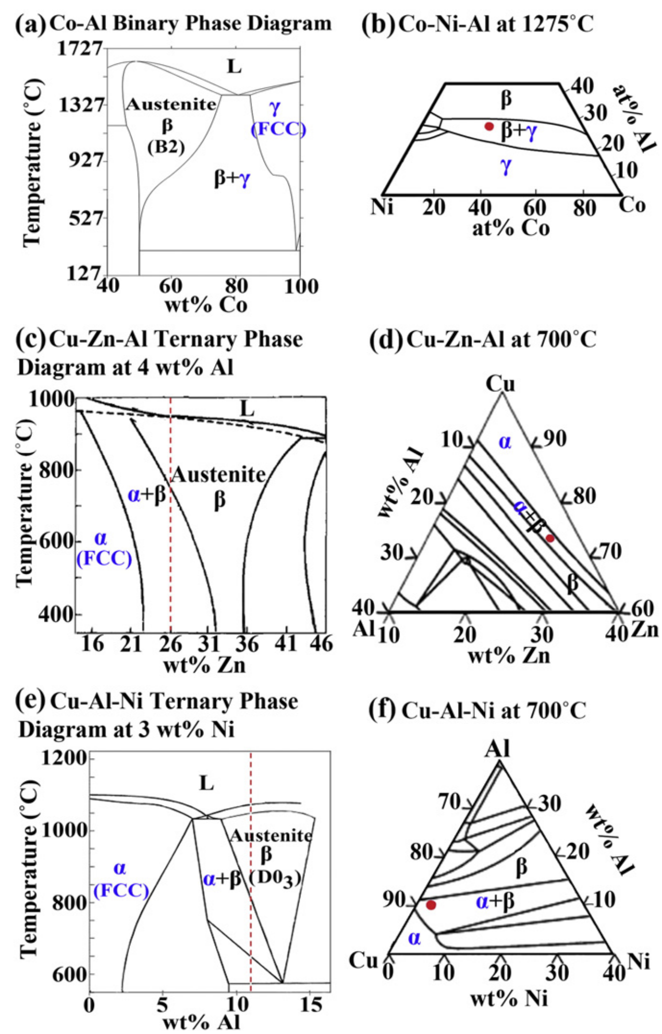


**Fig. 2.** (Color online) (a) Co–Al phase diagram [62]; (b) A Co–Ni–Al isothermal section [30]; (c) Cu–Zn–Al phase diagram at 4 wt.% Al [63] with 26 wt.% Zn shown as a dashed red line; (d) A Cu–Zn–Al isothermal section [64]; (e) Cu–Al–Ni phase diagram at 3 wt.% Ni [41] with 11 wt.% Al shown as a dashed red line; (f) A Cu–Al–Ni isothermal section [64]. The compositions of present alloys are shown as red dots in (b), (d), and (f).