Acta Materialia 124 (2017) 79–92

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Origin of zero and negative thermal expansion in severely-deformed superelastic NiTi alloy

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ARTICLE INFO

Article history:
Received 16 September 2016
Received in revised form
19 October 2016
Accepted 21 October 2016
Available online 4 November 2016

Keywords:
Severe plastic deformation
Shape memory alloys
Nanocrystalline microstructure
In situ transmission electron microscopy (TEM)
Zero and negative thermal expansion

ABSTRACT

We have investigated the physical origin of anomalous in-plane thermal expansion (TE) anisotropy leading to invar-like behavior and negative TE in nanostructured NiTi sheets manufactured via severe cold-rolling. The roles of grain size (GS), crystallographic texture, thermally-induced phase transformation, and intrinsic (lattice level) TE of austenite (B2) and martensite (B19′) phases on the macroscopic TE behavior are addressed. It is shown that by controlling the cold-rolling thickness reduction and heat-treatment temperature the coefficient of thermal expansion (CTE) can be controlled in a wide range from positive ($\alpha \sim 2.1 \times 10^{-5}\ K^{-1}$) to negative ($\alpha \sim -1.1 \times 10^{-5}\ K^{-1}$) via in-plane anisotropy of TE. A very small CTE of $\alpha \sim -5.3 \times 10^{-7}\ K^{-1}$ (invar-like behavior) in a wide temperature window of 230 K (353 −123 K) is obtained at an angle of 33.5° to the rolling direction (RD) of the severely cold-rolled sheet. TEM and XRD studies show that the microstructure underlying such anomalous TE behavior consists of a mixture of B2 nano-grains and retained/residual deformation-induced martensite and that the observed anomalous TE anisotropy is due to the intrinsic anisotropic TE of residual martensite. The invar-like behavior is the result of the cancellation of the positive TE of austenite phase with the negative TE of residual martensite along 33.5° to the RD. A simple rule of mixture model incorporating the intrinsic TE of B2 and B19′ lattices and the texture coefficients of the sample is proposed which successfully captures the anomalous in-plane TE anisotropy. The discovery of high dimensional stability over a wide temperature window along with temperature insensitive non-hysteretic linear superelasticity of the severely-deformed NiTi opens up a new route for designing stable SMAs for applications in ragged environments.

1. Introduction

The temperature-dependence of dimensions, usually referred to as thermal expansion (TE), is an intrinsic feature of metallic materials that arises from atomic bonding considerations [1]. Such temperature-dependence of dimensions, especially in the presence of large temperature variations or temperature gradients, limits the application of metallic materials to narrow temperature windows. For example, the difference in coefficient of TE (CTE) between substrate and thin films creates internal stress that affects the physical, electrical and thermal properties of the thin films [2–4]. In bridges, railroad tracks, and pipelines the TE has to be compensated by expansion joints. In high-precision instruments such as standard rulers and clocks where high dimensional stability of the components is required, materials with low TE (LTE) or even zero TE (ZTE) are employed. In recent years, there has been a significant growth of interest in developing materials showing Negative TE (NTE), LTE, and ZTE from both practical and theoretical points of view [5]. Several material systems showing NTE, LTE, and ZTE (tailorable TE) have been developed in which the value of CTE can be tailored to a specific value by chemical composition modification [6–12].

Shape memory alloys (SMAs) undergoing a thermoelastic first-order martensitic phase transformation (PT) are well-known in

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http://dx.doi.org/10.1016/j.actamat.2016.10.054
1359-6454/

medical, aeronautical, and MEMS applications [13,14]. Recently, it has been reported that SMAs can exhibit tailorable TE via manipulating their microstructure. Kainuma et al. first reported that moderately cold-rolled Cu-Zn-Al SMA shows CTE varying from 0 to $15 \times 10^{-6}\ K^{-1}$ [15,16]. Later, the tailorable TE was reported in Ti-23Nb-0.7Ta-2Zr-O (TNTZ) Gum metal alloy after moderate cold-rolling reductions [17,18]. Kim et al. investigated the effect of nanodomains on the LTE/ZTE of as-rolled Gum metal with chemical composition of Ti-23Nb-0.7Ta-2Zr-1.2O (at%) [19] and attributed the LTE/ZTE to compensation of vibrational lattice strain via growth of nanodomains during cooling [20]. However, others have attributed the LTE of Gum metal to the strain glass mechanism [21]. Monroe et al. proposed a universal mechanism leading to existence of NTE/ZTE in materials undergoing thermoelastic martensitic PT [22]. Using NiTiPd, CoNiGa, and TiNb as model alloys they argued that the TE anisotropy is directly linked to the crystallographic relationship between the austenite and martensite lattices [22]. Recently, Hao et al. reported tailorable TE in Ti–15Nb–2.5Zr–4Sn alloy due to nano-scale concentration modulation via phase separation [23]. Hence, it is noted that the mechanism of tailorable TE (LTE/ZTE/PTE) in SMAs is scattering and different scenarios have been proposed. For NiTi SMAs with the most widespread applications, there is no systematic work available on the existence of tailorable TE and its relationship with the microstructure remains unexplored.

In this study, we investigate the in-plane TE anisotropy of NiTi sheets (Ti-50.6 at.% Ni) manufactured via severe cold-rolling and controlled heat treatment. We report the existence of tailorable TE via in-plane anisotropy in the as-rolled and moderately heat-treated sheets. We show that the value of linear CTE is controllable between $\alpha = +21 \times 10^{-6}\ K^{-1}$ and $\alpha = -11 \times 10^{-6}\ K^{-1}$ and a near ZTE ($\alpha = -0.53 \times 10^{-6}\ K^{-1}$) can be achieved along 33.5° to the rolling direction (RD). The intrinsic TE behavior of B2 and B19′ structures and the corresponding TE matrices in the temperature range from 50 to 400 *K* are measured. The physical origin of the obtained tailorable TE is investigated using *in-situ* cooling TEM and *in-situ* XRD and a simple model of TE anisotropy is proposed that satisfactorily captures the observed NTE/ZTE/PTE behavior. The results suggest that the superelastic NiTi can be employed as a tailorable TE material without the need to modify its chemical composition. The combination of temperature-insensitive non-hysteretic superelasticity [24] along with high dimensional stability offers the severely-deformed superelastic NiTi alloy as suitable candidate for applications in ragged environments.

2. Materials and experiments

2.1. Materials

Polycrystalline superelastic NiTi sheets with chemical composition of Ti-50.6 at.% Ni and initial thickness of 1.524 mm were purchased from Johnson Matthey Company. The as-received sheets were annealed at a temperature of 1073 K (800 °C) for 1 h and quenched in water. Sheets with dimensions of $30 \times 1.524 \times 100\ mm^3$ were sandwiched in stainless steel sheets and cold-rolled in a 4hi cold-rolling mill set (YoshidaKinen Company) to thickness reductions of 42%, 50%, and 60%. The 50% rolled sheets were heat treated at temperatures of 1073 *K* for 30 min (referred to as 1073-30 sheet hereafter), 973 *K* for 5 min (973-5), and 623 *K* for 20 min (623-20). The 42% rolled sheet was annealed at 523 *K* for 60 min (523-60). The above heat treatments result in a range of microstructures with different features such as GS [24], defect density, texture [25], and different volume fraction of residual martensite as well as different superelastic properties [26,27].

2.2. Thermal expansion (TE) measurements

The role of microstructure on TE behavior was studied by a high-resolution thermal mechanical analyzer (TMA 402 F1/F3 Hyperion) from NETZSCH Company. Rectangular bars with dimensions of $18 \times 2.84 \times 0.60\ mm^3$ were cut along different angles to the RD (0°, 22.5°,33.5°,45°,67.5° and 90°) as shown in Fig. 1a. The specimens were heated up to 353 *K* with a heating rate of 10 *K/min*, held for 10 min for temperature uniformity, and then cooled down to 123 *K* using a cooling rate of 2 *K*/min with LN_2 cooling system. The macroscopic thermal strain was calculated as $l(T)-l_0/l_0$ where l is the length at each temperature and l_0 is the length at 353 *K*. Note that for clear illustration of PTE/ZTE/NTE response l_0 is chosen at 353 *K*.

2.3. Texture measurements

The texture of the as-rolled and heat treated sheets was studied by measuring the incomplete (110), (200), and (211) pole figures (PFs) of the parent austenite phase (B2) using a Rigaku XRD machine with Co Kα radiation source equipped with a 2-axis goniometer. The PFs were measured in the $15^o < \alpha < 90^o$ and $0^o < \beta < 360^o$ with an incident slit of 5 mm, α step of 1.5°, and β speed of 63 *deg/s*. In the as-rolled sheets the background was measured sufficiently away from the diffraction profiles due to broadened diffraction peaks. The defocusing was corrected using a plasma-atomized NiTi powder [28]. The Orientation Distribution Function (ODF) and transformation texture calculations were performed with MTEX package [29].

2.4. In-situ cooling TEM

A JIB-4000 Focused Ion Beam (FIB) was used to fabricate thin foils with thickness of less than 80 nm for *in-situ* TEM observations.

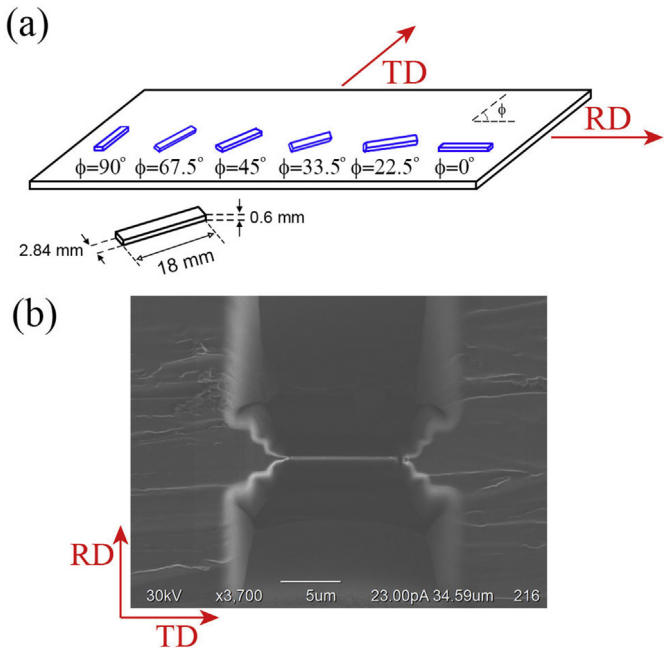

Fig. 1. (a) Schematic of the rectangular bars cut along different angles to the RD (φ) of the sheets for TE anisotropy measurements by TMA and (b) a typical SEM image of the thin foils fabricated by FIB for *in-situ* TEM observations.