Acta Materialia 142 (2018) 181–192

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

The role of W on the thermal stability of nanocrystalline $NiTiW_x$ thin films

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ARTICLE INFO

Article history:
Received 24 July 2017
Received in revised form
23 September 2017
Accepted 24 September 2017
Available online 26 September 2017

Keywords:
Shape memory alloys
Nanocrystalline
Grain boundary segregation
In-situ transmission electron microscopy

ABSTRACT

This paper investigates the effect of minority W additions on the thermal stability of nanocrystalline NiTi thin films. The films were produced in an amorphous state, and the addition of W was found to increase the activation energy for crystallization and lead to finer grain sizes after crystallization. In the crystallized films, W was observed to both segregate to the NiTi grain boundaries and to phase separate into fine precipitates; together these effects contribute to the stability of the nanocrystalline state up to 1200 °C. Using in-situ transmission electron microscopy, grain growth was observed concomitantly with coarsening of W precipitates, indicating that a primary mechanism for stability is Zener pinning by the W precipitates. At the same temperature where coarsening begins to occur rapidly, grain boundaries were also observed to undergo a transformation to thick, amorphous complexions. Monte Carlo simulations showed that W segregation to grain boundaries increases with temperature, which contributes to an increased rate of coarsening and loss of stability against grain growth.

1. Introduction

Due to excellent work output per unit volume and ultralow fatigue [1], NiTi-based shape memory alloy (SMA) thin films are increasingly used in micro-machines as micromanipulators and fluid micro-valves [2]. Controlling the phase transformation properties, such as thermal hysteresis [3] and mechanical hysteresis [4], are key aspects to improving the performance of NiTi SMAs. From a microstructure design perspective, most research to date has focused on meeting the so-called compatibility condition by tailoring the chemical composition of SMA thin films [3]. The control of grain size as an influential microstructural parameter has recently received increased attention due to the emergence of novel properties when grain sizes are in the nanocrystalline regime, where the martensitic phase transformation is observed both experimentally and theoretically to occur in a fundamentally different fashion [4–8]. There are a number of promising properties that have been observed in nanocrystalline SMAs: a small and vanishing thermal hysteresis (during thermally-induced phase transformations) for high speed microactuators [9], small and vanishing mechanical hysteresis (during stress-induced phase transformations) for ultra-fast superelasticity [10,11], stable superelasticity over a wide temperature window for extreme environments [4], improved non-isothermal cyclic stability [12], improved resistance against cyclic dislocation activity [13], and exceptional dimensional stability over a wide temperature range [14].

Retaining a nanocrystalline grain size during heat treatment and thermal cycling presents a serious challenge, as nanocrystalline materials tend to undergo rapid grain growth at elevated temperatures due to the high volume fraction of grain boundaries [15,16]. Nanocrystalline NiTi has been observed to undergo rapid grain growth at 900 °C by Mousavi et al. [17], with the grain size increasing from 25 nm to 0.1 μm in just one hour of annealing. In cases where abnormal grain growth occurs, the time and temperature required for rapid grain growth can be even lower [18].

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https://doi.org/10.1016/j.actamat.2017.09.056
1359-6454/

The instability of the nanocrystalline state affects processing of NiTi SMA thin films, which are generally fabricated by magnetron sputtering from elemental targets in the amorphous state followed by heat-treatment above the crystallization temperature (~400–450 °C [19,20]) to form a polycrystalline structure [21]. However, due to a relatively low nucleation rate and fast growth [22] the crystallized films typically have grain sizes on the order of a few microns [20]. Certain processing techniques have successfully reduced the grain size of the crystallized films to be on the order of hundreds of nanometers, for instance by rapid annealing [23,24] or using films of smaller thickness [19], but producing nanocrystalline NiTi from amorphous films remains challenging.

Introducing additional alloying elements into NiTi is a promising route for grain refinement and thermal stability of fine grain sizes. Alloying can increase the stability of a nanocrystalline material against grain growth in two ways: by increasing the activation energy for grain boundary motion, for instance through Zener drag of the solutes themselves, by Zener pinning due to a second phase, or by decreasing the grain boundary energy through solute segregation to the grain boundary. Which of these mechanisms is relevant, if any, depends on the alloy selected and the relative thermodynamic preferences for forming a second phase, dissolving into the nanocrystalline matrix, and segregating to the grain boundary [15,25–33].

The considerations for thermal stability in nanocrystalline NiTi alloys are more complex than most alloys that have been modeled to date, which are primarily binary, immiscible alloys. In the case of NiTi with a third, added stabilizing element, the nanocrystalline matrix is an intermetallic and the effect of the alloying element on thermal stability requires a ternary model capable of capturing ordering as well as grain boundary segregation. Empirically, a few alloying elements have been found to lead to smaller grain sizes and improved thermal stability in NiTi thin films. In Cu-doped Ni–Ti thin films, Callisti et al. [34] observed that the average grain size decreased substantially with increased Cu content; transmission electron microscopy (TEM) measurements revealed that Cu segregated to the grain boundaries which was likely responsible for the observed stability. However, the average grain size was still around 200 nm when alloyed with 17% Cu, which means Cu does not have a strong enough effect to produce stable nanocrystalline NiTi thin films. Buenconsejo et al. [9,35] and Kaur et al. [36] studied the effects of alloying with W and found a reduction in the grain size with increasing W content. However, unlike in the Cu-doped films, the grain sizes observed were in the nanocrystalline regime, around 25 nm [9,36], and the grain size was found to be stable after annealing for 1 h at 700 °C. X-ray diffraction (XRD) measurements revealed BCC W precipitates in NiTi, which suggests that Zener pinning may play a role in the thermal stability of nanocrystalline NiTi–W, but an understanding of how W interacts with grain boundaries is necessary to attain a complete picture of the thermal stability of this alloy.

In this work, we studied the evolution of amorphous NiTiW thin films through the crystallization and grain growth processes at different W concentrations and annealing temperatures, in order to better understand the role that W plays from both kinetic and thermodynamic perspectives. Annealing experiments were performed using differential scanning calorimetry (DSC) and TEM/EDS measurementswere used to study the effect of W on the crystallization and grain growth processes at different temperatures and W concentrations. These experiments were accompanied by *in-situ* TEM up to 1200 °C in a C_s-corrected TEM to study second phase formation, coarsening, and grain boundary segregation in real time. Thermodynamic Monte Carlo simulations were performed to help explain the observed microstructural features and thermal stability. We then used this understanding to draw general conclusions for important considerations for the thermal stability of ternary nanocrystalline alloys and nanocrystalline alloys with an intermetallic matrix phase.

2. Materials and experiments

2.1. Thin film fabrication

Commercial high purity Ni, Ti, and W targets were used for the sputtering. $NiTiW_x$ thin films were co-sputter deposited on a 10 μm water-cooled Cu foil with a Carousel-type RF magnetron sputtering system (L-350S-C, Canon ANERVA) at a base pressure of better than 5.0×10^{-4} Pa, Argon pressure of 0.5 Pa, and rotational speed of 50 rpm. The total sputtering time was 36 h resulting in a film thickness of ~9 μm. The alloy composition was adjusted by varying the applied RF power to each target. In this regard, the Cu-foil temperature and the applied RF powers were adjusted to prevent the samples from crystallizing during sputtering. In total seven thin films with chemical compositions of $Ni_{50.9}Ti_{49.1}$, $Ni_{50.3}Ti_{48.8}W_{0.8}$, $Ni_{50.9}Ti_{47.9}W_{1.2}$, $Ni_{50.9}Ti_{43.8}W_{5.3}$, $Ni_{52.4}Ti_{39.7}W_{7.9}$, $Ni_{49.4}Ti_{37.7}W_{12.9}$, $Ni_{50.9}Ti_{28.8}W_{20.3}$ were sputtered. The chemical composition was measured by an energy dispersive X-ray fluorescence spectrometer (EDX-1300, Shimadzu).

2.2. DSC and XRD measurements

The thin films were detached from the Cu substrate by immersing them in a HNO_3+ H_2O (50-50) solution and cleaned with acetone and ethanol. To investigate the effects of W on the crystallization process, isochronal and isothermal DSC measurements were conducted using a Netzsch 404 F1 and a Perkin Elmer PYRIS Diamond DSC. For the isochronal measurements, samples with a weight of ~5 mg were heated up to 600 °C at heating rates of 10, 20, 40, 60, and 80 °C/min. For the isothermal tests, samples were heated up to the desired temperature with a heating rate of 500 °C/min and kept at that temperature until reaching a stable and flat heat flow signal. A second cooling/heating cycle was applied to obtain the base line. Room temperature XRD measurements were carried out with a Rigaku SmartLab 9 kW XRD instrument equipped with a Cu$K\alpha_1$ radiation source ($\lambda = 0.154056$ nm). XRD diffractograms were recorded in the range $20° < 2\theta < 120°$ with a step size of 0.02°/step and scan speed of 10°/min. The film samples were set on a Si single crystal non-diffracting sample holder using a small amount of silicone grease.

2.3. TEM observations

Microstructural observations were performed by transmission electron microscopy on a JEOL JEM-2100F. For each film, disks with a diameter of 3 mm were punched from five different locations on the wafer, cleaned with ethanol, and thinned for electron transmission at a temperature of −167 °C using a cryogenic precision ion-polishing system (PIPS). To analyze heterogeneity in chemical composition and grain boundary segregation, scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS) was used. To observe processes in real-time, *in-situ* heating experiments were performed in a cold field-emission gun JEM-ARM200F TEM microscope equipped with double C_s correctors. Samples were first thinned with a focused ion beam (FIB) and further thinned with a PIPS for better electron transparency. A Wildfire sample holder with a Nano-Chip sample carrier from DENSsolutions was used to heat up the sample inside the TEM. $Ni_{49.4}Ti_{37.7}W_{12.9}$ was heated to 1000, 1100, and 1200 °C with a heating rate of 100 °C/min. The time required for the sample temperature to become stable was below 30 s. After TEM imaging,