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Elastically confined martensitic transformation at the nano-scale in a multifunctional titanium alloy

H.L. Wang [a], Y.L. Hao [a, *], S.Y. He [a], T. Li [b, c], J.M. Cairney [b], Y.D. Wang [d], Y. Wang [e, f], E.G. Obbard [g], F. Prima [h], K. Du [a], S.J. Li [a], R. Yang [a]

[a] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, 110016, China
[b] Australian Centre for Microscopy and Microanalysis, University of Sydney, Sydney, NSW, 2006, Australia
[c] Institute for Materials and Materials Research Department & ZGH, Ruhr-Universität Bochum, Universitätsstraße 150, 44780, Bochum, Germany
[d] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing, 100083, China
[e] State Key Laboratory for Mechanical Behavior of Materials and Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, 710049, China
[f] Department of Materials Science and Engineering, Ohio State University, Columbus, OH, 43210, USA
[g] Department of Electrical Engineering and Telecommunications, University of New South Wales, Sydney, NSW, 2052, Australia
[h] PSL Research University, Chimie ParisTech–CNS, Institu de Recherche de Chimie Paris, Paris, 75005, France

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ABSTRACT

A martensitic transformation (MT) is a typical first-order diffusionless crystal structural change with strong autocatalysis like avalanche at a speed of sound propagation. This unique characteristic, however, is undetectable in some multifunctional titanium alloys. Recently, a nano-scale elastically confined MT mechanism was proposed because a nano-scale Nb modulation in a Ti-Nb based alloy was observed. Here we analyze the elastic confinement in details and its induced novel properties in a wide temperature range. The statistical analyses of atom probe tomography (APT) data confirm the existence of the nano-scale Nb concentration modulation. The synchrotron X-ray diffraction (SXRD) profiles demonstrate that the nano-scale Nb modulation causes weak diffuse scattering, as evidenced by the extreme broad diffraction bands. The tensile tests find a critical temperature of ~150 K, where the critical stress to induce the MT and Young's modulus reach the minimum and the superelastic strain reaches the maximum (~4.5%) and keeps constant as the temperature decreases further to <4.2 K. To reveal these abnormal behaviors of the MT, the Born criterion governing the elastic stability of cubic crystal is modified by introducing an elastic confinement term and a new Clausius-Clapeyron relationship is established to evaluate the elastically confined MT. The results are consistent with the experimental findings, including the solely stress-induced (no thermally induced) reversibility.

1. Introduction

It has been well-known that the thermoelastic MT is the underlying mechanism of shape memory and superelastic effects of crystalline solids [1]. The recently developed multifunctional titanium alloys and non-martensitic shape memory alloys (SMAs) [2–7], however, suggest that the MT may not be the sole origin of these effects. Several novel reversible deformation mechanisms besides the MT, including strain glass transition [2,3], giant fault [4], large scale lattice distortion [5,7], as well as nanodisturance and dislocation loops [8] have been proposed. Of course, these new mechanisms have been challenged by the conventional MT mechanism because the MT has been detected in these materials. For example, the β (bcc) to α" (orthorhombic) MT has been confirmed experimentally in several multifunctional titanium alloys including the Gum Metal and Ti2448 alloy [9–11].

The above debate suggests two strategies to reveal the origin. On one hand, these mechanisms would be operative in advance of the MT. This was confirmed by an in-situ observation of Ti2448 alloy that three reversible mechanisms of the nanodisturbance, the dislocation loop and the MT are triggered in turn with the increase of the applied stress [8]. On the other hand, the novel mechanisms would couple with the MT. This is possible because the homogeneously nucleated lattice distortion is along the shear direction of the MT [8,12]. Now, the question is how to couple these

* Corresponding author. Tel.: +86 24 8397 8841; fax: +86 24 2390 2021.
E-mail address: ylhao@imr.ac.cn (Y.L. Hao).

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mechanisms with the MT so as to achieve some novel properties [4,13], which are in sharp contrast with those in typical SMAs such as NiTi [1].

Many factors alter the behavior of the MT, including composition, point defects, precipitates, grain boundaries, pre-deformation and phase separation in the parent phase [1]. The situation is more complicated for the β type titanium alloys because the β phase (bcc) is a high temperature phase which is thermally stable above 900 K in general for the developed alloys [14,15]. Thanks to the sluggish nature of the diffusional transformation from the β phase to the α phase (hcp) [14,15], the β phase can be kept metastable at room temperature and even lower during cooling in some alloys containing large amount of β stabilizers such as Nb and Mo [1]. Upon cooling, however, phase transformations taking place in the parent phase may alter completely the behavior of the MT. For example, precipitation of the ω phase [15–17] and development of nano-scale oxygen modulation in some alloys containing large amount of interstitial oxygen atoms [16,17] were found to lead to some novel behaviors of the MT such as the negative temperature dependence of the critical stress to induce the MT [18,19].

To explore the novel reversible deformation mechanism of these multifunctional titanium alloys, Ti2448 (abbreviated from its composition of Ti-24Nb-4Zr-8Sn in weight percent) would be a good model material due to the following reasons: First, it is free of athermal ω [6], or at least its formation is much weaker as compared to others β type titanium alloys [14]. Secondly, it has normal oxygen content of typical titanium alloys and is free of oxygen modulation [6]. Finally it has the intrinsic character of novel nonlinear elasticity, which is caused by continuous elastic softening with increased stress [5].

As mentioned above, the reversible nanodisturance and dislocation loop in Ti2448 are nucleated homogeneously before the trigger of the MT. Furthermore, the α" martensite is localized abnormally in ~2.5 nm equiaxed regions [8], unlike micron-scale internally twinned martensitic plates commonly observed in SMAs [1]. These reveal that its MT may be confined by a nano-scale heterogeneous microstructure. The nano-scale ω precipitation and oxygen modulation would satisfy the requirement, particularly the latter has been found in oxygen-rich titanium alloys. However, both are absent in Ti2448 alloy as mentioned above. Recently, our APT analysis found a nano-scale concentration modulation of Nb [13], which is most likely produced by spinodal decomposition in the β phase at elevated temperature before the MT. A nano-scale elastically confined MT mechanism was proposed to explain some unprecedented properties such as superelasticity (SE) from <4.2 K to 500 K and fully tunable thermal expansion, from positive, through zero, to negative, from <4.2 K to 625 K [13].

The current work focuses on the nano-scale 3D concentration modulation in Ti2448 and its effect on properties in a wide temperature range from 4.2 K to 398 K. By introducing an elastic confinement term into the typical equations characterizing the MT, the nano-scale elastically confined MT is evaluated for a comparison with the experimental results. These results reveal that this reversible mechanism combines some advantages of both the conventional MT mechanism in the typical SMAs such as NiTi and the elastic deformation mechanism in the typical elastic stable materials such as pure metals. This would open a door to tune the reversible MT so as to obtain some unexpected properties of the typical SMAs.

2. Experimental

An ingot of Ti2448 alloy with a diameter of 380 mm was fabricated by vacuum arc melting by using a Ti-Sn master alloy and pure Ti, Nb and Zr as raw materials. The chemical compositions obtained by wet chemical and gas analyses are presented by both weight and atomic percent in Table 1. The ingot was hot-forged at 1123 K to form round bars 55 mm in diameter and then hot-rolled at 1073 K to 12 mm in diameter.

The uniaxial cyclic loading and unloading tensile tests were conducted on a MTS-SANS CMT 5000 machine equipped with a CryoLab low temperature system and an Epsilon 3542 low temperature extensometer by using rod samples with a gauge section of 5 mm in diameter and 25 mm in length at an initial strain rate of 2.5×10^{-4} s^{-1}. The tests were carried out at temperatures ranging between 4.2 and 398 K, which were controlled by a KEITHLEY 2000 MULTIMETER system. To measure the elongation and the reduction in area, some samples were loaded cyclically until fracture.

The APT samples were cut into small rods 0.5 mm in diameter and 20 mm in length, polished in a solution containing $HClO_4$ (5%), 2-butoxyelethnol (35%) and methanol at 233 K under a voltage of 50 V, and then sharpened with a Zeiss Auriga FIB until the tip radius was less than 100 nm. The prepared samples were field evaporated by a Cameca LEAP 4000× SI instrument. The analyses were carried out in laser pulsing mode at 23 K, a target evaporation rate of 5 ions per 1000 pulses, a pulse rate of 250 kHz, a laser energy of 80 pJ and a laser spot size of ~2 μm. The wavelength of the UV laser was 355 nm. The APT data were reconstructed and analyzed using IVAS 3.6.6™ software. To create iso-concentration surfaces of these Nb-rich and Nb-lean domains, a traditional marching cube algorithm was employed, which interpolates linearly between adjacent grid points to identify points on the surfaces. From this set of points, a set of triangles is constructed in order to make the surface continuous. To confirm the existence of the nano-scale Nb modulation, here we give the error analysis of the APT data according to the method in Refs. [20,21].

The SXRD analyses were performed on beamline ID-11-C at Advanced Photon Source (APS), Argonne National Laboratory (ANL) using 113 keV x-ray with a wavelength of 0.0112 nm and beam size of 2500 μm^2. A 1.5 mm thick band shaped sample was exposed with the longitudinal axis perpendicular to the X-ray beam. Diffraction patterns were collected by a 2D digital detector.

3. Results

3.1. The nano-scale Nb modulation

Optical observation showed the as hot-rolled Ti2448 alloy has a deformed microstructure (Fig. 1A). In spite of difficulty in identifying grains from the optical microstructure, it can still be estimated that averaged size is ~5 μm. TEM analysis found that the alloy has a fine microstructure sized in ~0.6 μm (Fig. 1B). The observed features are termed as subgrains because the small misorientation angels are less than 2° in general. Selected area diffraction analysis showed it has single β phase microstructure (the inset in Fig. 1B) [22].

Recent 3D APT analyses revealed that the cooling from the high temperature β phase field leads to a nano-scale heterogeneity in composition via an isostructural spinodal decomposition [13]. This creates a nano-scale Nb modulation consisting of the interpenetrating Nb-rich and Nb-lean domains that are 2–3 nm in size and are approximately equiaxed in shape [13]. Six examples of 3D

Table 1
Chemical composition of Ti2448 alloy.

	Nb	Zr	Sn	O	Ti
wt%	24.2	3.96	8.10	0.13	Bal.
at.%	15.1	2.54	3.99	0.48	Bal.