Scripta Materialia 133 (2017) 70–74

Contents lists available at ScienceDirect

Scripta Materialia

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

Regular article

Tracing the coupled atomic shear and shuffle for a cubic to a hexagonal crystal transition

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

[a] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 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] Department of Electrical Engineering and Telecommunications, University of New South Wales, Sydney, NSW 2052, Australia
[e] European Synchrotron Radiation Facility, Grenoble 38043, France
[f] Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, TX 75080, USA
[g] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology, Beijing, 100083, P.R. China
[h] Department of Materials Science and Engineering, Ohio State University, Columbus, OH 43210, USA
[i] PSL Research University, Chimie ParisTech–CNS, Institu de Recherche de Chimie Paris, Paris 75005, France

ARTICLE INFO

Article history:
Received 20 January 2017
Received in revised form 12 February 2017
Accepted 16 February 2017
Available online xxxx

Keywords:
Titanium alloy
Phase transformation
Burgers mechanism
Shear
Shuffle

ABSTRACT

Tracing the rearranged atoms in the first-order phase transformation is unrealistic due to the discrete structure change. Here we report that, by tuning a nano-scale decomposition in a titanium alloy, the bcc crystal distorts successively toward the hcp crystal by keeping an orthorhombic symmetry. Thus, the shear-shuffle relationship is traced experimentally to enrich the well-known Burgers mechanism. Our results reveal also that the successive tuning on crystal structure at the atomic level leads to some novel properties which are unexpected from the discrete phase transformations.

Solid-solid phase transformations typically undergo a discrete structure change from a parent to a product crystal via atomic shear and/or shuffle. The discrete nature raises a question of how to characterize these rearranged atoms. Thanks to the well-known orientation relationship of the parent and product crystals, the phase transformation pathways have been established geometrically, for example, the Burgers relationship/pathway of body centered cubic (bcc) and hexagonal close packed (hcp) crystals [1]. However, these geometrical models exclude the detailed information such as the sequence and correlation of the coupled atomic rearrangement [2–8]. Here gives a strategy to trace the structural change by tuning a discrete transformation into a continuous transition wherein the parent crystal is distorted successively toward the product crystal. This letter demonstrates for the first time that, by tuning a nano-scale concentration modulation via spinodal decomposition in a titanium alloy, the discrete bcc-hcp transformation can be continuous and the successive atomic shear and shuffle components are traceable by in-situ measurements.

The discrete bcc-hcp transformation occurs in many solids such as Fe, Ti, Zr and their alloys [9,10]. The Burgers mechanism outlines a coupled shear and shuffle components [1–3]: (1) a shear component of a bcc {110} plane, consisting of an elongation along [110] and compression along [100] perpendicular directions, to make perfect hexagons (Fig. 1a); and (2) a shuffle component of the adjacent {110} planes to get a stacking sequence of the hcp crystal (Fig. 1b). The former results in an increase of the lattice parameter b/a ratio from 1.414 of the bcc crystal to 1.732 of the hcp crystal, while the ideal hcp crystal forms as the c/a ratio increases from 1.414 to 1.633. The latter leads to the Wyckoff position y coordinate decreasing from 0.25 to 0.167. Our measurements will provide solid evidence that these values vary continuously from the bcc to hcp, in sharp contrast with the sudden changes observed in the discrete transformations [4–6].

The above exploration was inspired by the recently-developed multifunctional titanium alloys with high strength and low elastic modulus [11,12]. Their continuous nonlinear deformation has attracted great attention and some reversible mechanisms besides the thermoelastic martensitic transformation (MT) have been proposed [13–16]. However, these have been challenged because a typical reversible MT, the β (bcc) to α″ (orthorhombic) MT, has been detected [15–17]. Our recent

* Corresponding author.
E-mail address: ylhao@imr.ac.cn (Y.L. Hao).

http://dx.doi.org/10.1016/j.scriptamat.2017.02.024
1359-6462/

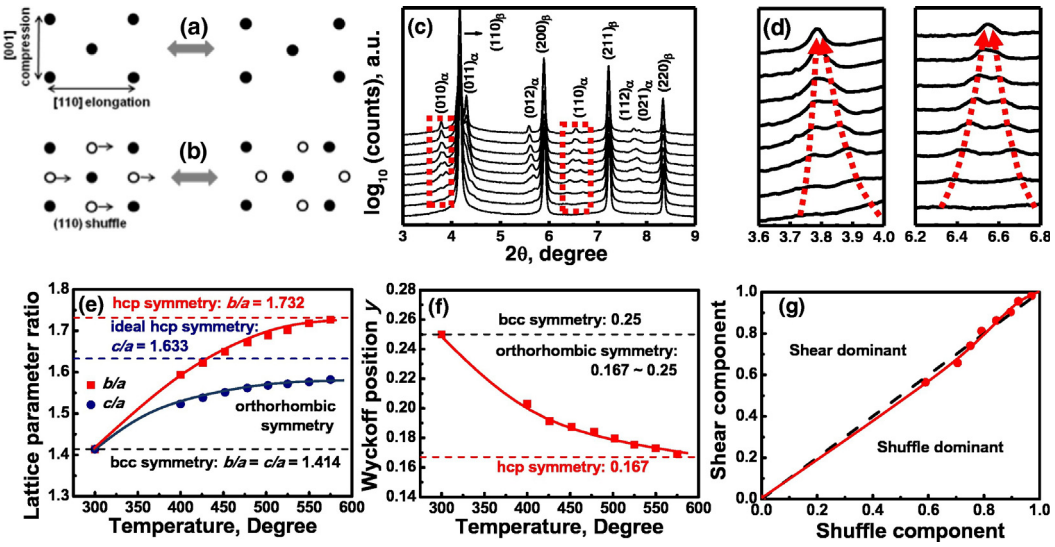

Fig. 1. In-situ SXRD analyses of the heated Ti2448 alloy. (a) and (b) Schematics of pure shear (a) and shuffle (b) components of the bcc-hcp transformation respectively. (c) Integrated 1D SXRD profiles recorded from 375 to 575 °C at an interval of 25 °C (from bottom to top). (d) The enlarged sections indicated by the dotted rectangles in (c) show the new diffraction peaks and their significant shifts indicated by the curved arrows as temperature increased. (e) and (f) The continuously varied lattice parameter ratios (e) and the Wyckoff position factor (f) from the bcc crystal to the hcp crystal under the restriction of an orthorhombic symmetry. (g) The unified shear and shuffle relationship (the details see text).

3D atom probe tomography (APT) analysis of Ti2448 alloy showed that it passes through an isostructural spinodal decomposition [18], which creates a nano-scale architecture consisting of the interpenetrated Nb-rich and Nb-lean domains. Since the Nb-rich domains are more stable, producing an elastic confinement on the MT in the neighboring Nb-lean domains, a nano-scale elastically confined MT mechanism was proposed [18]. Aided by the elastic confinement, the alloy is multifunctional over much wider temperature range than the typical shape memory alloys such as NiTi, for example, it exhibits the superelasticity 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 [18].

In this letter, we show that the spinodal decomposition is enhanced gradually as the alloy is heated and aged in the β (bcc) and α (hcp) two-phase field. Both in-situ and ex-situ measurements reveal that, under the elastic confinement of the Nb-rich β domains, the Nb-lean β domains pass through a successive crystal distortion from bcc to hcp via the coupled atomic shear and shuffle by keeping an orthorhombic symmetry. Thus, the shear-shuffle relationship outlined by the Burgers mechanism is traced in experiment. Additionally, the above successive tuning on crystal structure at the atomic level leads to some novel properties which are unexpected from the discrete phase transformations.

The alloy has a nominal composition Ti-15Nb-2.5Zr-4Sn in atomic percent and is abbreviated as Ti2448 from its weight percent composition Ti-24Nb-4Zr-8Sn. An ingot was hot-forged at 850 °C and hot-rolled at 800 °C to 12 mm in diameter. The ingot has actual composition of 15.1Nb, 2.54Zr, 3.99Sn and 0.48O in atomic percent and 24.2Nb, 3.96Zr, 8.10Sn and 0.13O in weight percent. In-situ synchrotron X-ray diffraction (SXRD) analysis was conducted on the high energy beamline ID15B of European Synchrotron Radiation Facility (ESRF) with a wavelength of 0.017048 nm. A cylindrical sample of 3 mm in diameter and 10 mm in length was heated from 25 to 575 °C at a rate of 3 °C/min and 2D diffraction patterns were recorded on a Pixium 4700 flat-panel detector. The patterns were analyzed with the whole pattern Rietveld method in the program package MAUD [19]. The APT samples were analyzed by a Cameca LEAP 4000× SI instrument and the data were reconstructed and analyzed using IVAS 3.6.6™ software [20]. The TEM study was conducted using a probe-corrected JEOL ARM200F atomic resolution analytical electron microscope operated at 200 kV, equipped with a high-angle annular dark field (HAADF) detector and an energy dispersive X-ray (EDX) detector. Uniaxial tensile tests were performed at a strain rate of $2.5 \times 10^{-4}\ s^{-1}$ on an Instron 5582 universal test machine using rod sample with a gauge section 5 mm in diameter and 25 mm in length. The stress–strain curves were recorded by a strain extensometer.

It is clear from the integrated 1D SXRD profiles (Fig. 1c) that the heated alloy has a single bcc phase up to 375 °C. As temperature increases further from 400 to 550 °C, the orthorhombic (orth) phase, as indexed by these new and weak peaks, forms from the bcc matrix with larger volume at higher temperature. At 575 °C, the orth phase is replaced by the hcp phase. Interestingly, the peak angles of the orth phase shift significantly until the formation of the hcp phase at 575 °C. Meanwhile, the bcc phase peak angles do not change significantly. To clearly show the continuous peak shift of the orth phase, two sections in Fig. 1c are enlarged and presented in Fig. 1d.

From the SXRD profiles in Fig. 1c, the lattice parameters of three kinds of crystals were calculated and the variations of their ratios (b/a and c/a) with temperature are plotted in Fig. 1e. Similarly, the calculated Wyckoff position factors (y) are presented in Fig. 1f. Since these new peaks in Fig. 1d become much weaker and broader at lower temperature, the early stage of bcc crystal distortion is untraceable. However, the slight distortion is estimated by extrapolating the measured data, which vary exponentially with temperature (see the curves in Fig. 1e and f). From this estimation we can conclude that the bcc crystal starts its distortion at 300 °C, with a small fitting error of ± 2 °C for the b/a and c/a ratios and the factor y.

Aided by the experimental data in Fig. 1e and f, the shear-shuffle relationship can be established (Fig. 1g). Following the typical definitions [1–3], both shear and shuffle are set as zero for the initial bcc crystal and unity for the finial hcp crystal. The shear is defined by a unified change of b/a ratio. To show the early stage of crystal distortion, the fitting data by the exponential curves in Fig. 1e and f are presented by a red curve in Fig. 1g. These results reveal that the shear and shuffle vary almost equally except weak shuffle and shear dominant at the start and the end respectively. This is in sharp contrast with the previous simulations to be strong shear or shuffle dominant [3,5,21].

The successively distorted bcc crystal can be detected by ex-situ TEM analysis. According to the Burgers mechanism, the shear component of a bcc {110} plane also reduces the characteristic angle θ between the two (110) diagonals from 70.53° to 60° to make perfect hexagons [3]. As it can be seen in the selected area diffraction (SAD) patterns in