Full length article

Exploring the concurrence of phase transition and grain growth in nanostructured alloy

Linke Huang, Weitong Lin, Bo Lin, Feng Liu[*]

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

A B S T R A C T

In nanostructured alloys, the concurrence of (solid-state) grain growth and phase transition is ubiquitously observed; however, due to the lack of kinetic evidences, the underlying physics of concurrence remains scarcely understood. In this study, for nanostructured Fe alloy as a model system, macro- and micro-scale characterizations for the concurrence were carried out using *in situ* X-ray diffraction and *in situ* high-resolution transmission electron microscopy (HRTEM). Macroscopically, the grain growth occurs and ceases before the end of phase transition, and microscopically, the concurrence of grain boundary (GB) and phase boundary (PB) migrations was certified as well. These experimental results, together with the *ex situ* HRTEM and molecular dynamics simulation, uncovered the interaction between GB and PB migrations, i.e., both velocity and direction of the PB migration are influenced when the PB interacts with the GB. On this basis, the concurrence was utilized to produce a new kind of heterogeneous and hierarchical microstructure (i.e., dual-phase bimodal nanostructure). The present findings, yield a deep understanding of the phase transition in nanostructured alloys, and further, demonstrate the potential usage of concurrence in manipulating the nanostructures for the development of nanostructured alloys.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Interfaces, such as grain boundary (GB) and phase boundary (PB), as basic constitutions in nanostructured (NS) materials, are origins of some unique properties for such materials, e.g., enhanced strength [1,2], poor thermal stability [3,4]. Therefore, understanding the mechanism of interface activities is beneficial to the optimization of mechanical properties or the increase of thermal stability, thus offering the potential for wide application of these materials. Grain growth and solid-state phase transition, as two crucially macroscopic phenomena of interface migrations, not only are common reactions when the NS materials suffer instability [3,4], but also serve as versatile accesses in manipulating the microstructures for fabrication of NS materials (for example, see Refs. [5—7]), thereby attracting extensive research interests.

The two solid reactions, for coarse-grained materials (>1 μm), often happen independently since the driving force of grain growth

(e.g., typically and roughly,[1] 0.01—0.1 kJ/mol in Fe alloys [8]) is sufficiently small as compared to that of phase transition (typical values as 0.5—3 kJ/mol from Refs. [9,10]). Whereas, for NS materials, the driving force of grain growth will increase at least one order of magnitude and then becomes comparable to that of phase transition. Furthermore, interestingly, for most engineering materials (see Fig. 1), the activation energy of GB migration is oftentimes lower than or comparable to that of PB migration. As thus, only if both thermodynamic and kinetic conditions are satisfied can grain growth and phase transition take place simultaneously in NS materials. On this basis, one may conclude that the materials at the lower right corner of Fig. 1 are ideal candidates for the above concurrence. The generality of concurrence can be exhibited by many experimental findings, such as, in W alloys [5], Cu alloys [6], Fe alloys [11,12], Ni alloys [13—15], TiO_2 [16—18], where the grain growth of parent phase is concomitantly involved in various kinds of phase transition processes (e.g., phase separation [5], GB

---

* Corresponding author.
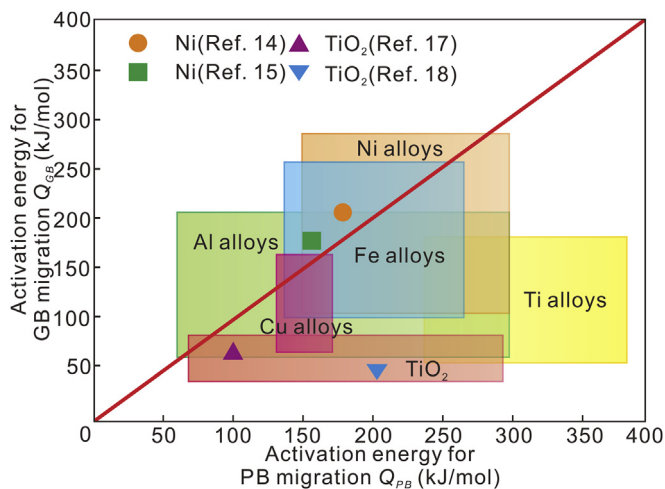E-mail address: liufeng@nwpu.edu.cn (F. Liu).

Fig. 1. Activation energies for GB and PB migrations of typical engineering materials. Phase transition can refer to allotropic transition (e.g., ferrite to austenite transition in Fe alloys, anatase to rutile in TiO_2), or precipitation (e.g., precipitation of Ni_3P in Ni alloys, precipitation of Al_2Cu in Al alloys). The whole region is divided into two parts by the red solid line where $Q_{GB} = Q_{PB}$. Materials which belong to the lower right corner where $Q_{GB} < Q_{PB}$, are preferable for the concurring solid state reactions. Detailed determination of general areas of Q_{GB} and Q_{PB} for typical materials is available in Supplementary Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

complexion [6], allotropic transition [11,12,16–18], precipitation [13–15]). In practice, the concurrence has been used in fabrication of desired microstructures, e.g., the formation of thermally ultra-stable nanotwins in NS Co-Ni alloy [19]. Yet, present studies [5,6,11–19] are primarily concentrated on the resulting microstructures arising from the concurrence, kinetic evidences for the concurrence have never been provided in NS alloys, and hence, the mechanistic understanding behind the physical phenomenon has not been elucidated. The main motivation of this work, therefore, is to explore the underlying physics behind the concurrence and to utilize the concurrence in tailoring the nanostructures.

Regarding the scientific interest and the technological importance of phase transition in steels [20], herein a typical body-centered cubic (bcc) to face-centered cubic (fcc) phase transition upon heating NS Fe alloys is studied as a model system. The concurrence of phase transition and grain growth in the NS $Fe_{91}Ni_8Zr_1$ (in atomic %) alloy (detail of alloy selection is in Section 2.1) is investigated with macroscopic and microscopic characterizations. The interaction between GB and PB migrations behind the concurrence is then elucidated. On this basis, we show that the concurrence of phase transition and grain growth can be applied to produce hierarchical dual-phase bimodal nanostructures (DPBNs), which are expected to find potential applications in optimizing the mechanical properties of NS alloys.

2. Material and methods

2.1. Material

Previous studies [21,22] in pure NS Fe and *in situ* X-ray diffraction (XRD) study in our work (Supplementary Fig. 1), indicate a loss of nanostructure due to catastrophic coarsening prior to bcc to fcc phase transition upon heating. Therefore, the strategy of alloying is adopted to retain the nanostructure. Extensive experiments [23,24], as well as the theoretical studies in our group [25,26], show that Zr can effectively mitigate grain growth in NS Fe-Zr alloys, whereas this efficiency is limited to a low or intermediate

temperature range (i.e., ~300–800 °C; see Supplementary Fig. 1). To avoid the deterioration of nanostructure prior to phase transition, besides the addition of Zr, it thus becomes inevitable to depress the phase transition point,[2] which can be realized by introducing Ni as an fcc-stabilizing element in Fe [27]. Moreover, the precipitation of secondary particles upon heating [12,23,24] is easily promoted with enhanced Zr concentration (e.g., 5 at.%), which will make the microstructure evolution complicated in present study. As thus, with all of these considerations in mind, $Fe_{91}Ni_8Zr_1$ was designed as a model alloy.

NS $Fe_{91}Ni_8Zr_1$ alloy, was prepared by high energy ball milling using pure Fe powder (purity 99.99 wt%), Ni powder (purity 99.95 wt%) and Zr powder (purity 99.99 wt%). 20 g of mixed powders were sealed in a stainless steel vial, and milled for 50 h under a high-purity Ar atmosphere, with 10 mL n-hexane as a process control agent. The ball to powder weight ratio was 10:1. After ball milling, microscale powders comprising uniform nano-structures of single bcc phase, were obtained.

2.2. In situ characterizations

The concurrence was investigated using *in situ* XRD experiment in the Bruker D8 Discover with Co K-alpha radiation, from room temperature to 1,000 °C with a heating rate of 30 K/min. To capture the kinetics of concurrence, two-dimensional detector was selected, with an exposure time of 1 s. The raw two-dimensional data was then converted into one-dimensional diffraction pattern by virtue of the commercial software EVA (Bruker). The instrumental broadening was determined by NIST Al_2O_3 sample. Evaluation of grain size, microstrain and phase volume fraction was conducted using the Rietveld method within the Topas software (Bruker) [28].

To study the interface migration behaviors, *in situ* high-resolution transmission electron microscopy (HRTEM) investigation was carried out using a DENSsolutions double-tilt heating holder at Tecnai G2 F20 instrument operated at 200 kV. Due to the size effect of foil samples in TEM [29], phase transitions often take place at lower temperatures for *in situ* TEM experiments than those for *in situ* XRD measurements. Therefore, in our study, a series of *in situ* TEM experiments at a lower magnification were conducted firstly to determine a proper temperature for *in situ* HRTEM observation and finally, 600 °C was selected. It is noted that, to minimize the thermal drift of sample, an isothermal heating for *in situ* HRTEM was used.

2.3. Molecular dynamics (MD) simulation

To further investigate the interface interaction, MD simulation using the LAMMPS [30] code was carried out as well. The interatomic interactions were described using the modified embedded-atom method (MEAM) potential for Fe developed by Lee et al. [31]. MD simulation was conducted using Nose-Hoover isothermal-isobaric (NPT) ensemble under zero pressure and 1,400 K and the time step was 1 fs. We used a sample with the X, Y, Z dimensions of 20 nm × 20 nm × 5 nm consisting of 25,641 atoms; an fcc nucleus was embedded at GB beforehand since this simulation concentrates on the interface interaction instead of phase nucleation. Periodic boundary condition was applied in X, Y and Z direction. To avoid the drifting of sample, the center-of-mass velocity was subtracted by adjusting the velocity of each atom. The Ovito [32] was employed in the visualization analysis. The hot

---

[2] Phase transition point is herein defined as the start temperature of phase transition.