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ScienceDirect

Acta Materialia 79 (2014) 37–46

Acta MATERIALIA

www.elsevier.com/locate/actamat

A kinetic Monte Carlo study of coarsening resistance of novel core/shell precipitates

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Received 2 May 2014; received in revised form 1 July 2014; accepted 3 July 2014

Abstract

A novel approach towards the design of coarsening-resistant nanoprecipitates in structural alloys was investigated by kinetic Monte Carlo (KMC) simulation. The approach is motivated by recent experimental results in Cu–Nb–W alloys showing that room temperature ion irradiation resulted in W nanoprecipitation, leading to exceptional stability of W-rich-core/Nb-rich-shell nanoprecipitates formed following thermal annealing (Zhang et al., 2013 [11]). Here, image simulations of atomically resolved scanning transmission electron microscopy are performed to establish that these W nanoprecipitates are highly ramified. Thermal precipitate coarsening in an A–B–C ternary alloy similar to Cu–Nb–W is then studied by KMC simulations, where the highly immiscible and refractory C solute atoms are initially distributed into fractal nanoprecipitates, or cores, which become coated by a shell of B atoms during elevated temperature annealing. Compared with nanoprecipitates generated by compact C cores, the ramified nanoprecipitates result in exceptionally high trapping efficiency of B solute atoms during thermal coarsening, and the efficiency increases with the cluster size. The KMC results are analyzed and rationalized by noting that, owing to the Gibbs–Thomson effect, when the curvatures of the shell of the precipitates are zero or negative, the microstructure is coarsening-resistant. Such morphology can be realized by facets, or by dynamic balance within positive, negative and zero curvatures.

Keywords: Copper alloys; Ion irradiation; Precipitation; Core/shell structure; Monte Carlo techniques

1. Introduction

Precipitation-hardening, or age-hardening, in metal alloys has been practiced for some 100 years [1,2], and it remains a cornerstone in the development of high-strength materials. Age-hardened alloys, however, are generally limited to relatively low-temperature applications, owing to their tendency to coarsen, particularly in systems containing nanoprecipitates. Various attempts have been made to stabilize these ultrafine microstructures, including creating core/shell structured precipitates [3–7] and adding finely dispersed oxide particles to the matrix [8,9]. Recently, a novel approach was demonstrated to stabilize a wide range of nanoprecipitates using energetic particle irradiation of dilute Cu–W-based alloys [10]. The method makes use of the facts that W is extremely immiscible with Cu, and its tracer diffusivity in Cu is very slow. In past experiments, the present authors used physical vapor deposition to create homogeneous alloys of $Cu_{100-x}W_x$ for $1.0 < x < 10$. Irradiation of these alloys, even at low temperatures, led to the nucleation of nano-W precipitates, roughly 1 nm in diameter. Computer simulations and analytical modeling [10] suggested that precipitation occurs locally within cascades during thermal spikes. Ternary alloys with composition near $Cu_{90}Nb_9W_1$ were also considered [11]. With Nb and W initially in solution, room

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http://dx.doi.org/10.1016/j.actamat.2014.07.010
1359-6454/

temperature ion irradiation leads to clustering of W atoms and W nanoprecipitates, while leaving the Nb largely unaffected. Subsequent annealing finally leads to the precipitation of Nb on the W clusters, forming novel core/shell structures. This method differs from typical core–shell synthesis [4–6] in that the core element W diffuses far more slowly in Cu than does the shell element Nb. These precipitates were found to be extremely coarsening-resistant, and it was hypothesized that the alloy stability arises from the extremely small mobility of W in Cu, coupled with the very strong trapping of Nb at W clusters.

Also different from the above-mentioned typical core/shell structures is the structure of the Nb–W precipitates. Whereas typical core/shell structures in metals are compact and have distinct core/shell interfaces, experimental observations [11] on the W clusters formed under irradiation suggest that they are ramified, having a very large ratio of surface area to volume. This conclusion was proposed to help rationalize the ultra-high trapping efficiency of the W clusters; the experiments showed that just 1.5 at.% W can trap 10 at.% Nb. The present work explores the nature of these irradiation-induced nanoprecipitates in more detail, using atomistic simulation methods to provide a more systematic understanding of the trapping efficiency and the coarsening resistance. Two simulation methods are employed. First, scanning transmission electron microscopy (STEM) images of the W clusters introduced by room temperature ion irradiation are simulated to verify that the clusters are indeed ramified. Kinetic Monte Carlo (KMC) simulation is then used to study the trapping of Nb by the W clusters. Together, these simulations verify that the ramified nanoprecipitate structure is the key ingredient for efficient trapping, and extreme coarsening resistance. Although this work is directly related to the present authors' experimental observations on metallic solids, they believe the general ideas can be applied to any systems provided that the components have similar interaction characteristics and there is a way to produce clusters with high area-to-volume ratios. In fact, in some polymer blends, co-continuous morphologies can be made coarsening resistant by adding nanostructures that spontaneously cluster within one phase [12], which is essentially employing ideas similar to those discussed here. In other work studying the pinning of phase separation in biological systems, such as the inhibition of the coarsening of the lipid raft phase in cell membranes [13], membrane bond proteins serve as immobile pinning sites, which prefer the lipid raft phase rather than the matrix phase, and a significant slow-down of lipid phase coarsening was observed.

2. STEM simulations

A past study on the Cu–Nb–W system showed that W atoms cluster and precipitate out of solution during room temperature irradiation with 1.8 MeV Kr ions, while Nb atoms remain dissolved. Fig. 1 illustrates this behavior; it shows a Z-contrast STEM image taken after irradiation.

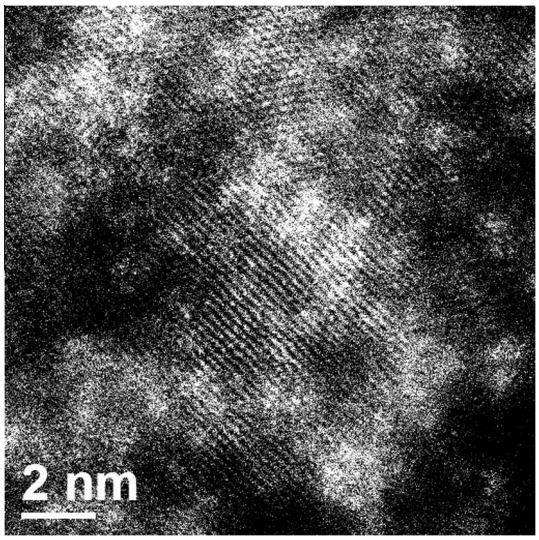

Fig. 1. Z-contrast STEM images showing the microstructure of the $Cu_{88.5}Nb_{10}W_{1.5}$ sample after room temperature irradiation. Bright regions are indicating the presence of W. Adapted from Ref. [11].

The bright areas indicate the W-rich precipitates in the sample. The structure of the precipitates in this image appears to be ramified; however, this possibility is explored more thoroughly using STEM image simulation. The simulations are performed assuming a $Cu_{99}W_1$ alloy with face-centered cubic (fcc) structure and with all W atoms in the form of clusters. Two groups of microstructures are considered: one with compact spherical W particles and the other with ramified W clusters. The ramified clusters are generated using a modified diffusion limited aggregation (DLA) algorithm, as described below. The sample size in the STEM simulation is $11 \times 11 \times 11$ nm. It should be noted that, since the images are two-dimensional (2-D) projections, overlapping of clusters in space can result in modified shapes in the pictures.

The DLA algorithm employed to generate the ramified clusters was modified from that originally introduced by Witten and Sander [14] in order to generate several clusters in one simulation cell at the same time. In this model, immobile W "seed" atoms are located at random sites. Then, one W atom is placed at a random lattice site not yet occupied by W, and it is allowed to randomly walk until becoming the nearest neighbor of a seed, where it attaches. New W atoms are added only after the preceding W atom has attached to an existing cluster. The process stops when the W concentration has reached the desired level. The average cluster size can be controlled by changing the number of seeds. The microstructure generated in this step is then used as input for the STEM simulation.

The STEM image simulation package used in this study is Zmult [15]. Zmult implements the multi-slice algorithm to simulate electron probe propagation by including electron dynamic scattering. Electron scattering of each slice is treated as the phase object, followed by propagation using the Fresnel propagator [16]. A Fast Fourier