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Chemical mixing and self-organization of Nb precipitates in Cu during severe plastic deformation

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Abstract

Severe plastic deformation (SPD) of Cu, Ag and Nb ternary alloys with average Nb concentrations of 5, 10 and 15 at.% and an Ag concentration of 10 at.% was studied using high resolution scanning electron microscopy, atom probe tomography and X-ray diffraction. Ball-milled powders were compacted, annealed at 600 or 950 °C and subsequently strained by high pressure torsion at room temperature. Ag redistributed homogeneously in the Cu matrix during SPD, but the Nb solubility increased by less than 1%. The Nb precipitates, moreover, self-organized into a patterned microstructure, whereby their sizes all fell within a narrow distribution, centered on ~20 nm. This size was independent of the initial microstructure for a given alloy and insensitive to the Nb concentration. The size was also insensitive to the method of shearing. Since Nb diffusion is negligible in Cu at room temperature, these results establish that SPD alone can induce compositional patterning in highly immiscible alloys. We discuss the mechanisms responsible for this behavior.
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Keywords: Self-organization; Severe plastic deformation; Micro-structure; Solubility

1. Introduction

The extension of solid solubilities in immiscible alloy systems during severe plastic deformation (SPD) has been widely studied in the past [1–6], and several general trends have been established. In alloys with low-to-moderate heats of mixing, such as Cu–Ag [3], Cu–Fe [1] and Cu–Co [6], SPD leads to complete solubility over the entire range of compositions. For alloys with very high heats of mixing, on the other hand, including Cu–Nb [7,8] Cu–Mo [7], Cu–Ta [9], Ni–Ag [4] and Fe–Ag [5], solubilities can be extended by only rather limited amounts. In both alloy types, these findings persist even when the deformation is performed at temperatures significantly below room temperature (RT) where vacancies are virtually immobile. Various explanations have been suggested for why immiscible alloys mix during SPD, and interested readers are referred to Refs. [10,11] for a discussion. Critical points from these works will be discussed later. The present work, however, is more concerned with why highly immiscible alloys do not homogenize completely, for which there has been much less consideration. The question is intriguing, since SPD leads to enormously high supersaturations of solute in all immiscible systems, illustrating that shear-induced chemical mixing indeed takes place. What is less clear is why the mixing stops. Different suggestions have been offered. For example, Zghal et al. suggested that when refractory precipitates become too small they no longer can be sheared [12]. Other models rely on thermodynamic arguments based on the Gibbs–Thomson equation [2], or the "effective temperature" model [5] of Martin [13]. In the present work we follow phase evolution during SPD of $Cu_{(90-x)}Nb_{x}Ag_{10}$ alloys, where $x = 5$, 10 and 15. We show that Ag indeed goes into solution in the Cu matrix, but that the Nb solubility is limited. Our principal finding, however, is that the system self-organizes to select a fixed length scale for the Nb precipitation that is

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independent of the initial size of the precipitates, and only weakly dependent on the alloy concentration. The length scale for phase separation is also insensitive to the method of shearing. We suggest that the reason for this behavior derives from the chemically biased motion of atoms during SPD which leads to nucleation and growth of new precipitates as the solubility is increased by shearing.

Self-organization in moderately immiscible alloys during SPD was first observed in kinetic Monte Carlo computer simulations [14], and demonstrated experimentally in Cu–Ag alloys [15]. The basis for the self-organization is a dynamic competition between shear-induced mixing and thermally activated diffusion [16,17]. The shear-induced mixing in moderately immiscible results in homogenization, while thermally activated diffusion causes precipitation. At low temperatures and high shearing rates, diffusion is suppressed and the mixing is enhanced, leading to homogenization of the alloy. At high temperatures and low shearing rates, the dynamic competition is reversed and precipitates tend to grow large. Self-organization occurs when these dynamics are of comparable strength, and derives from a subtle difference in the way atoms moved during thermal diffusion and shear mixing. The details of the model can be found elsewhere [17]. We point out here that the current experiments are performed at room temperature and thermally activated diffusion is largely suppressed. Consequently, the self-organization reported in the present work cannot be explained by this same mechanism.

While we study ternary alloys of Cu–Ag–Nb, the primary focus of this work is the behavior of Cu–Nb during SPD. Ag additions facilitate this study as they provide two important benefits. First, Ag is only moderately immiscible with Cu and hence it serves as a marker for monitoring the deformation and mixing in the Cu lattice, i.e. Ag has been shown to mix with Cu similarly to the mixing of Cu atoms in pure Cu [18,19]. At the same time, Ag is highly immiscible with Nb and hence it should not much influence the mixing between Nb with Cu. The second purpose of the Ag addition is practical. Part of our sample preparation method employs ball-milling (see Section 2). Cu and Nb powders, however, undergo severe cold welding onto the milling tools and do not form the fine powders that are necessary for SPD. The addition of 10 at.% Ag prevents cold welding in this and other Cu alloy powders.

Shear mixing of Cu–Nb has been studied in the past, but the results have been unclear in regards to understanding shear mixing in highly immiscible alloys. Most studies have been concerned with the co-deformation of Cu and Nb and changes in the two-phase morphology during wire drawing [8] or accumulative roll bonding [20,21]. These studies typically employ strains less than ~10, and thus mixing is confined to a few nanometers [10,19]. In one study using drawing of Cu–Ag–Nb wires, the mixing at Cu–Nb interfaces was measured [10]; however, we distinguish our work from this study as it examined the initial stages of shear mixing, whereas the current work is primarily concerned with the steady state microstructure. In other work, shear mixing of Cu 5–20 at.%. Nb alloys was investigated using ball-milling experiments [7,22,23]. The work in Ref. [7] had suggested that up to 10 at.% Nb could be dissolved in Cu during low temperature milling; however, little detailed examination of the microstructure was reported. In the present work, we employ both high pressure torsion (HPT) and ball-milling methods to deform our samples and use a combination of high resolution scanning and transmission electron microscopy, X-ray diffraction (XRD) and atom probe tomography (APT) to follow the microstructural evolution of Cu–Ag–Nb alloys from their initial stages of mixing through to steady state.

2. Methods

The ball-milling experiments were performed at RT using a Spex 8000 mixer mill using Cr-steel milling tools and an initial ball-to-powder weight ratio of 25:5 g. The Cu, Ag and Nb powders were mixed in the ratio 80:10:10 and 85:10:5; the average particle sizes of the initial powders were ~30 μm. The powders were then milled until steady states were obtained, up to 15 h. After ball-milling, mixed powders were then transferred to a hot press while still in an argon atmosphere, and compacted at 300 °C using a load of ~1 GPa under a high vacuum (2×10^{-6} Pa). Densities greater than 93% of the theoretical value were achieved. The samples were then annealed at 600 °C for up to 5 h, cut into 300 μm thick disks with electric discharge machining (EDM) and polished for unconstrained HPT experiments. Unconstrained indicates that the disk can spread between the roughened anvils during straining. Our research on Cu–Ag alloys indicates that the deformation is nearly homogeneous using this geometry, but that it is not using constrained HPT [19]. The HPT shearing was performed in a cyclic mode, i.e. rotating the anvils back and forth by 90°, with an applied pressure of 4.5 GPa and a rotation speed of 1.2 rpm. The number of back-and-forth cycles ranged from 3 to 25.

XRD measurements were used to determine the grain size and alloy solubility. A PANalytical/Philips X'pert MRD system was used to examine different radial positions (strain) on the specimen; the beam size was 1 mm × 1 mm. The precipitate size was determined by scanning electron microscopy (SEM) in secondary emission mode, using a FEI Helios 600 focused ion beam (FIB). SEM images were obtained immediately after cleaning the surface with a low energy ion beam at glancing angle. The ability to image the specimens, in situ, in the FIB, was very valuable for resolving the small Nb precipitates. High resolution transmission electron microscopy (HRTEM) was used to examine the atomic structure and grain size of the sheared alloy. APT using a Cameca LEAP 4000X Si atom probe was performed to provide information on the local chemistry and precipitate morphologies. These samples were prepared by FIB milling. APT tips with tip radii of ~40–50 nm were analyzed at 60 K using laser pulsing