Available online at www.sciencedirect.com

Acta Materialia 54 (2006) 2605–2613

www.actamat-journals.com

Nanocomposites stabilized by elevated-temperature ball milling of $Ag_{50}Cu_{50}$ powders: An atom probe tomographic study

Fang Wu [a,b], Dieter Isheim [c], Pascal Bellon [a,*], David N. Seidman [c]

[a] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304, W. Green Street, Urbana, IL 61801, USA
[b] Department of Materials Science and Engineering, University of Connecticut, Storrs, CT 06269-3136, USA
[c] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108, USA

Received 4 October 2005; received in revised form 25 January 2006; accepted 26 January 2006
Available online 3 April 2006

Abstract

$Ag_{50}Cu_{50}$ alloys were prepared by high-energy ball milling at 393, 423, and 453 K. Atom probe tomography was used to characterize the microstructure and the local composition of the milled powders. The dynamical competition between the atomic mixing forced by milling and the phase separation promoted by thermodynamic driving forces results in the self-organization of the microstructure into compositional patterns. Three-dimensional atom reconstructions show that the length-scale of the compositional patterns increases with increasing milling temperature, from about 1 nm at 393 K to 3–5 nm at 423 K and 5–10 nm at 453 K. Interfaces of the nanocomposites produced by milling at 423 and 453 K, analyzed using the proxigram technique, are found to be quite diffuse, ∼2 nm. The results are discussed in the light of a new analysis of the chemical mixing forced by plastic deformation, and its role in the stabilization of compositional patterns.

Keywords: Mechanical alloying; Three-dimensional atom probe; Copper alloys; Nanostructure; Self-organization and patterning

1. Introduction

Over the last three decades, powder processing by ball milling has attracted wide practical interest as it offers a simple but powerful way to synthesize non-equilibrium phases and microstructures, from nanograin materials to extended solid solutions, amorphous phases, chemically disordered compounds, and nanocomposites [1–5]. A crucial step toward a broader use of this synthesis route resides in our ability to select the milling parameters that will lead to the desired non-equilibrium phases or nanostructures.

In the case of moderately immiscible alloy systems, it has been demonstrated that full solid solutions can be stabilized by low-temperature, high-energy ball milling; examples include Ag–Cu [6,7], Cu–Co [8], and Cr–Mo [9]. A decade ago, it was proposed that the sustained plastic deformation of powders could be accommodated by the glide of dislocations, and that this sustained dislocation glide would be responsible for forced atomic mixing [10]. The recent observations of high dislocation densities in solid solutions forced by ball milling [11,12] provide support for this idea. At higher milling temperatures, where thermal diffusion is no longer frozen, using generic kinetic Monte-Carlo (KMC) simulations on a rigid lattice, it was shown that the dynamical competition between forced mixing and thermally activated decomposition leads to self-organization of the microstructure into compositional patterns [10]. Recent molecular dynamics simulations and kinetic modeling have revealed a determinant factor in triggering the self-organization reaction: the efficiency of the mixing forced by dislocation glide increases with the scale of composition heterogeneities, while thermally activated vacancy migration gives rise to diffusion coefficients that are scale independent [13]. As a result, there should be a

---

[*] Corresponding author. Tel.: +1 217 265 0284; fax: +1 217 333 2736.
E-mail address: bellon@uiuc.edu (P. Bellon).

1359-6454/$30.00 © 2006 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2006.01.042

crossover length, below which thermally activated phase separation dominates, and above which forced mixing is predominant. This crossover length is likely to correspond to the characteristic scale of the compositional patterns [13]. The spontaneous formation of nanocomposites during elevated-temperature ball milling has now been confirmed in Ag–Cu powder mixtures [14,15]. In agreement with the driven alloy theory [16,17], which was initially developed by Martin for alloys under continuous irradiation [18], it has been experimentally established that these nanocomposites are stable dynamical steady states, and that one can induce transitions from one steady state to another by varying the milling parameters; for instance the milling intensity [19,20] or the milling temperature.

One remarkable prediction of the KMC simulations is that the scale of the compositional patterns in steady state should increase continuously as the milling temperature increases. If confirmed, this property would offer a simple and powerful means to tune the length-scale of nanocomposites synthesized by ball milling. This could be important for the optimization of these nanocomposites since many nanomaterial properties display a strong length-scale dependence. We present a test of this tunability of the decomposition length-scale for the Ag–Cu system. Our choice is motivated by the large body of results already available for this system. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) results showed that a wide range of non-equilibrium structures can be obtained by varying the milling temperature, from nearly random solid solutions at cryogenic temperatures to states that are partly decomposed at temperatures above ~373 K [6,21]. Conventional atom probe field ion microscopy (APFIM) confirmed that cryo-milled powders are brought into a nearly random solid solution, while milling at 503 K produces nanocomposites with decomposition scales around 30 nm [14]. Transmission electron microscopy (TEM) indicated that, at this elevated milling temperature, the Ag–Cu powders undergo dynamic recrystallization during milling, and the scale of the nanocomposites, ~30 nm as measured by energy dispersive X-ray spectroscopy with scanning TEM, appears to be largely controlled by recrystallization [15]. At lower milling temperatures, $T \leqslant 453$ K, recrystallization is not observed, but the decomposition takes place at length-scales smaller than typical TEM foil thicknesses (~20 nm), and it is thus not possible to image compositional patterns in concentrated alloys due to averaging of the composition field through the foil thickness. It is not possible to use conventional APFIM either, since the analyzed material comes from a small cylinder, 1–2 nm in diameter, along the tip axis. As a result, in the absence of a priori information on the scale and the morphology of the compositional patterns, one cannot distinguish an inclined but sharp interface from a diffuse interface perpendicular to the tip axis.

In this article, we take advantage of the recent development of atom probe tomography (APT) [22–24] to overcome these limitations and to analyze in three dimensions Ag–Cu nanostructures stabilized by milling at moderately elevated temperatures, that is, from 393 to 453 K. In Section 2, the experimental procedures employed to ball mill the powders and prepare APT specimens are described. APT results are presented in Section 3, and discussed in Section 4.

2. Experimental

Ball milling of Cu and Ag powders was performed following the procedure described in detail by Klassen et al. [6]. Powders of Cu and Ag were mixed to achieve the desired nominal (atomic) composition of $Ag_{50}Cu_{50}$. All elevated-temperature millings were preceded by a 24 h milling treatment at ambient temperature, ~315 K, so as to alloy the initial powders. Results are reported for powders milled for 5 h at three temperatures: 393, 423, or 453 K. Ball-milled powders were systematically characterized using XRD and DSC. These results have already been reported elsewhere [6,14], and they are therefore not presented here. Additionally, the milled powders were extensively analyzed using conventional APFIM [14] and TEM [11,15].

APT was used to analyze the composition of the ball-milled powders at the atomic scale in three dimensions. Samples were prepared following the method we introduced [14,25]. This method, which involves cold swaging of the powders in a soft Cu tube, followed by conventional electrochemical polishing, is designed to minimize any alteration of the microstructure of the powders during sample preparation.

The three-dimensional atom probe used in this study was an energy compensated position-sensitive atom probe [26]. Analyses were carried out with a 1.5 kHz pulse repetition rate with a 19–20% pulse fraction and maximum operating DC and pulse voltages of 16 and 3 kV, respectively. The residual vacuum in the chamber was about 1.3×10^{-10} Pa, and the specimen temperature during analysis was held at either 60 or 80 K. Ions were collected from a total of eleven specimens, with six of them containing enough ions (>300,000) to provide meaningful datasets (Table 1). Analysis of the datasets was performed using Adam1.5 [27,28], a three-dimensional visualization and data analysis software developed at Northwestern University, and dedicated to the analysis of APT data.

From a mass spectrum collected by the atom probe, ions with mass-to-charge ratios ranging between 31 and 34, 62 and 70, 78 and 86, 90 and 98 amu are identified as Cu atoms in the reconstructed atom maps, since they correspond to Cu^{2+}, Cu^{+}, CuO^{+}, and $CuCO^{+}$ ions, respectively. Ions with mass-to-charge ratios ranging between 105 and 113, 124.5 and 128.5, 134 and 138 amu are identified as Ag atoms, as they correspond to Ag^{+}, AgH_2O^{+}, and $AgCO^{+}$ ions, respectively. As seen from Table 1, for the five specimens analyzed in detail below, specimens 1B, 2B, 2C, 3B, and 3D, more than 80% of the detected ions are recognized as originating from Ag or Cu atoms. Occasionally, nanoscale copper oxide precipitates were detected