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Structural and Chemical Nanoscale Electron Microscopy Characterization of Ag-Cu Ball Milled Powders

P. Bellon,* S. Zghal,** M. J. Hÿtch,*** J.-P. Chevalier,*** R. Twesten,* F. Wu****

* Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL 61801
** Department of Physics, University of Monastir, Monastir, Tunisia
*** Centre d'Etudes de Chimie Métallurgique, CNRS, 15 rue Georges Urbain, Vitry-sur-Seine, 94407 France
**** Metallurgy and Materials Science, University of Connecticut, Storrs, CT 06369

We present a study of nanostructured Ag-Cu powder material obtained by variable temperature ball-milling. The microstructural characterization is carried out using a wide variety of transmission electron microscopy (TEM) techniques, ranging from conventional dark-field imaging, selected area diffraction and energy dispersive X-ray spectrometry (EDS) to scanning TEM high-angle dark-field imaging (HAADF), nanodiffraction, and high resolution imaging (HREM) coupled with geometric phase image method [1].

First, when ball-milling is performed at low temperatures, typically room temperature and below, Cu and Ag are forced into solid solutions at steady-state [2]. The analysis reveals that the material is organized a various scale. The material is heavily textured and is comprised of elongated units, about 100 nm in length and 30 nm in width. While the main crystallographic orientation is preserved in these regions, local variations of orientation are detected by nanodiffraction. The geometric phase image method reveals that the textured grains are comprised of subunits that are rotated with respect to each other by angles ranging from a few to fifteen degrees (Fig. 1). Furthermore, it is shown that these local rotations are sometimes accommodated purely elastically, and sometimes partially plastically. In contrast, the lattice parameter is shown to be constant throughout the samples (Fig. 1c). A very large average density of dislocations, about 10^{16} m^2, is measured from the geometric phase images. Diffraction and STEM-EDS indicate that the sample is chemically homogeneous, in agreement with our previous atom probe characterization.

Second, when ball milling is performed at elevated temperatures, Ag-Cu nanocomposites are synthesized at steady-state [3]. Nanocomposites can also be obtained by annealing at elevated temperature chemically mixed and cold-worked powders obtained by room temperature milling. Upon increasing the milling temperature, two new steady-states are observed: a decomposed but unrecrystallized state at moderate temperatures, from 120 to 180˚C, and a decomposed and recrystallized state at elevated temperature, 230˚C. In the unrecrystallized state, the decomposition takes place at a scale smaller than the sample thickness (20 nm). In the recrystallized state, equiaxed grains of average size 15 to 20 nm are present, and, probably as a result of this recrystallization, the scale of decomposition is larger, about 30 nm, so that it can be directly imaged by STEM-EDS (Fig. 2a). In the annealed state, it is similarly found that, now keeping the annealing temperature fixed at 230˚C, a chemically decomposed but unrecrystallized state is obtained after short annealing time (1 h), while at longer times (5 to 10 h) discontinuous recrysallization takes place, producing grain of average size 40nm. The decomposition scale is accordingly larger, about 75 nm (Fig. 2b).

The two main conclusions of this work are that i/ low temperature milling produces a heavily textured and defective material, contrary to the expected well defined nanograins, and ii/ nanocomposites can be directly synthesized by moderate or elevated temperature milling or annealing. The first point lends support to the idea that dislocation activity is responsible for the forced chemical mixing of these immiscible elements. The second point suggests that ball milling, under appropriate conditions, provides a simple and direct process to synthesize nanocomposites.

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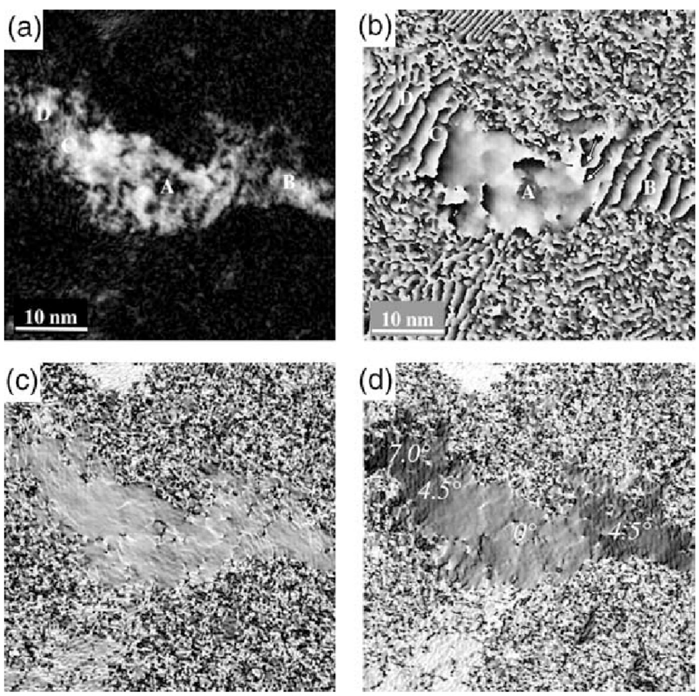

FIG. 1 Amplitude and phase analysis of a high resolution image of a cryo-milled sample. (a) amplitude image, (b) phase of (111) lattice fringes, (c) grayscale map of local lattice parameter, (d) grayscale map of local rotation. Notice the existence of 4 sub-units, A, B, C, D. Sub-unit C is chosen as the reference for calculating the local rotations.

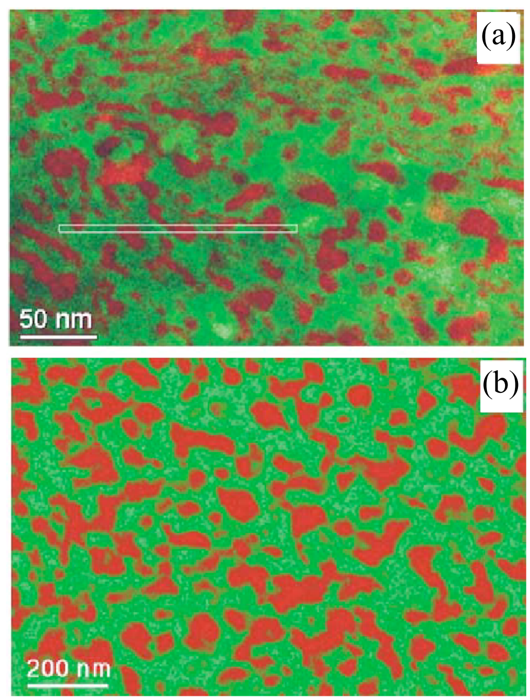

FIG. 2 STEM-EDS chemical maps of nanocomposites obtained (a) by elevated temperature milling, (b) by annealing. Red (light gray) and green (dark gray) correspond to Cu and Ag, respectively.

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