



Forced atomic mixing during severe plastic deformation: Chemical interactions and kinetically driven segregation

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Abstract

Shear mixing of the ternary alloy system Ag–Cu–Ni during ball-milling and high-pressure torsion was investigated to elucidate the effects of chemical interactions on phase formation. First, ball-milling of pure Ni with homogeneous Ag₆₇Cu₃₃ alloy powders at room temperature (RT) was studied for average Ni atomic concentrations of 4%, 9%, 15% and 25%. Additional samples with an average composition of Ag₅₀Cu₂₅Ni₂₅ were ball-milled at ~ -15 °C or subjected to high pressure torsion at ~ -125 °C. X-ray diffraction and atom probe tomography measurements showed that Cu largely transferred from the Ag–Cu alloy phase to the Ni-rich phase at all temperatures, but that Ag and Ni did not significantly intermix. The Cu concentration in the steady state, moreover, was surprisingly higher in the Ni-rich phase than in the Ag-rich phase, and it was further enriched at the interphase boundary, even at -125 °C. High-resolution transmission electron microscopy revealed that the sizes of the Ni/Cu precipitates and the grain size of the Ag-rich matrix were reduced to a few nanometers during RT or cryo-ball-milling, which is much finer than those observed after ball-milling of Cu–Ag or Ni–Ag binary powders. These findings illustrate that chemical effects can play an important role in phase formation during severe plastic deformation, but they also show that other kinetic factors can influence the final microstructure as well.

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1. Introduction

The extension of solid solubilities in immiscible alloys during severe plastic deformation (SPD) has been widely reported in a number of previous studies [1–12]. For example, Cu–Fe and Ag–Cu, which have heats of mixing at the equimolar composition of $\Delta H \approx 13$ kJ mol⁻¹ [1] and 6 kJ mol⁻¹ [3,13], respectively, display nearly complete ranges of solid solubility during ball-milling when the

milling is performed near room temperature (RT) or below [1,4,5]. These results are often rationalized theoretically within the framework of “driven alloys” [14]. The idea is that SPD forces a ballistic relocation of atoms, such that alloy components flow down gradients in their concentration. As long as the temperature is below that necessary for thermally activated diffusion to restore equilibrium, the alloy will tend to homogenize. In contrast, the Ni–Ag system, which has a value of $\Delta H_m > 20$ kJ mol⁻¹ at the equimolar composition [15], remains two-phase on a nanometer length scale during ball-milling, even during cryo-milling [6,16]. This observation contrasts strongly with those for Cu–Ag and Cu–Fe, and thus indicates that

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atomic motion during SPD is not completely ballistic in such alloy systems. Other examples of incomplete mixing behavior in metals have been reported for Fe–Ag [17], Cu–Nb and Cu–Mo (see e.g. Refs. [8,9]) and Cu–Ta [18], all of which display high heats of mixing, similar to Ni–Ag.

Several atomistic computer simulations have been performed to study the mechanisms that control SPD in binary alloys [12,19–21]. In regard to understanding the lack of mixing in the Ni–Ag system, molecular dynamics (MD) simulations have indicated that forced mixing during SPD is not ballistic in highly immiscible systems, but rather the mixing is “guided” in this case by chemical interactions [12,19]. At low temperatures, these effects were found significant for values of $\Delta H_m > \sim 20 \text{ kJ mol}^{-1}$, while at high temperatures, the effects became noticeable for $\Delta H_m = 10 \text{ kJ mol}^{-1}$ [12]. The present authors point out that the effects observed by MD at high temperatures are not associated with thermal diffusion mediated by atomic exchanges with vacancies, but rather with a temperature-dependent bias in the atomic exchanges during shearing [12]. More generally, however, decomposition of an initially homogeneous immiscible alloy during shearing at elevated temperatures occurs by two mechanisms: guided forced mixing and thermal diffusion [12,22].

Despite this qualitative agreement between experiments and computer simulation on the controlling mechanisms in driven alloy systems, there is little direct experimental evidence that shear mixing is influenced by the heat of mixing in absence of diffusion. In fact, the mechanisms of shear mixing remain controversial [7,23]. The observation that systems such as Ag–Ni or Cu–Mo do not form solid solutions during low temperature milling might be explained, for example, by localization of deformation, since the shear moduli of Ni and Ag are 80 GPa and 30 GPa, respectively, and those for Mo and Cu are 122 GPa and 48 GPa. These large differences might cause localized plastic flow in the “softer” phase, in this case Ag, with few dislocations crossing the Ag/Ni interfaces. Indeed, Da Pozzo et al. have suggested that mechanical properties can influence shear mixing [20]. It has also been suggested that thermal diffusion plays a role in the phase separation, even at relatively low temperatures, for example as expressed in the “effective temperature” model [17] or the Gibbs–Thomson effect [2]. The present work shows that the limited enhancements of solubilities in driven Ag–Ni alloys indeed derive from a chemical bias in the atomic exchanges driven by shearing, and are not due to localized plastic deformation or thermal diffusion. This is demonstrated using Cu as a tracer element in the Ag–Ni system under SPD. Since Cu will dissolve in either Ag or Ni during ball-milling, the investigation of the ternary alloy Ag–Cu–Ni system can be used to monitor whether shear mixing occurs in both the Ni and Ag phases. A more surprising result of this work is that Cu does not partition equally between the Ni-rich and Ag-rich phases, even though chemical biasing should be insignificant, i.e. Cu completely homogenizes with both Ni and Ag during shear deformation in binary systems. In this study,

ball-milling experiments are performed at RT and at $\sim -15^\circ\text{C}$ on several alloys in the Ag–Cu–Ni system. High-pressure torsion (HPT) experiments were also performed at $\sim -125^\circ\text{C}$ on initially phase separated $\text{Ag}_{50}\text{Cu}_{25}\text{Ni}_{25}$ alloys. Lastly, as a further manifestation of a chemical bias during shearing, it is demonstrated that Cu segregates to interfaces between Ni-rich and Ag phases. Segregation is particularly strong at higher temperatures, when some thermal diffusion takes place, but it also occurs at temperatures where vacancies are immobile.

2. Methods

The initial procedure was to ball-mill Ag and Cu to form $\text{Ag}_{66.7}\text{Cu}_{33.3}$ alloys and subsequently mill these alloys with pure Ni powders. Milling was performed in a controlled Ar atmosphere at RT or below using a Spex 8000 mixer mill with Cr-steel milling tools and an initial ball-to-powder weight ratio of 25:5. The temperature rise of the vial during RT milling was $\sim 25^\circ\text{C}$. X-ray diffraction (XRD) showed that the Cu–Ag alloys became homogeneous during milling at RT and that the steady-state grain size was $\sim 8 \text{ nm}$. These results are consistent with previous work [3]. Ni powders were then added to the Ag–Cu alloys and ball-milled at RT up to 25 h; the microstructure at this time had again reached steady state. Some powders were mixed by reversing the alloying order, i.e. Cu and Ni were first milled and the alloy powder subsequently mixed with Ag. Additional powders were milled at -15°C . In this case, cold N_2 gas was directed over the vial in the shaker mill. The temperature was measured inside the vial after the shaker mill and cooling gas were turned off; thus -15°C represents a maximum possible temperature during milling. Lastly, HPT was applied to phase-separated $\text{Ag}_{50}\text{Cu}_{25}\text{Ni}_{25}$ disk-shaped samples at $\sim -125^\circ\text{C}$. These samples were prepared by hot pressing previously RT ball-milled powders; pressing was performed in vacuum at $\sim 300^\circ\text{C}$ under a pressure of $\sim 1 \text{ GPa}$. These samples were nearly fully dense ($>95\%$), and they showed no open porosity.

Structural characterization of the milled powders was carried out using XRD, high-resolution transmission electron microscopy (HRTEM) and atom probe tomography (APT). For the diffraction measurements, a Siemens-Bruker D5000 X-ray diffractometer for powder diffraction was employed, and a PANalytical/Philips X’pert MRD system was employed to examine different radial positions (strain) on the HPT specimen; the beam size was $1 \times 1 \text{ mm}$; Cu $K\alpha$ irradiation was used with both diffractometers. Diffraction peaks were fitted to a pseudo-Voigt function using MDI Jade XRD pattern processing software. Grain sizes were obtained using the Scherrer method. The solubility limits in the Ag matrix were obtained from the shifts in the Bragg peak position, using the calibration from Ref. [24]. HRTEM was used to verify the grain sizes obtained from XRD. HRTEM specimens were prepared using focused ion beam (FIB) sputtering by a FEO Helios 600 FIB. Lattice constants of independent grains were also

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