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Competition between precipitation and dissolution in Cu–Ag alloys under high pressure torsion

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ABSTRACT

Severe plastic deformation (SPD) always leads to the strong grain refinement in the materials. Logically, in two- and multiphase alloys SPD has to cause the fragmentation and dissolution of precipitates in a matrix. However, it has been observed recently, that, contrary to this generally accepted viewpoint, SPD can lead also to the decomposition of supersaturated solid solution. In this work we analyze for the first time (both experimentally and theoretically) the competition of these simultaneous processes can take place, namely (1) the dissolution of precipitates and (2) decomposition of supersaturated solid solution with precipitation of a second phase. As a result, a dynamic equilibrium between these two processes appears, and a certain steady-state concentration in a solid solution is reached.

In this work we study the high pressure torsion (HPT) of a two-phase Cu–3.9 at. % Ag alloy in two different states: (i) as-cast consisting of a (Cu) solid solution with diluted 1.9 at.% Ag and another 2 at.% Ag as fine silver precipitates and (ii) an almost homogeneous solid solution with diluted 3.9 at.% Ag obtained by homogenization at $T = 780$ °C, 900 h and subsequent water quenching. HPT at room temperature causes the partial dissolution of precipitates in the as-cast samples and partial decomposition of the solid solution in homogenized samples. After HPT, the solute concentration in the matrix is the same in both samples (about 2.9–3.0 at.% Ag). Thus, it does not depend on the initial state and is higher than the equilibrium solubility limit at the HPT temperature. This concentration is equal to solubility limit at the effective temperature of $T_{\mathrm{eff}} \approx 680$ °C.

We also proposed the model describing the dynamic equilibrium between dissolution and precipitation in HPT. Assuming that HPT fixes the composition at matrix-precipitate interfaces, we show that HPT-enhanced diffusive transport of species is the process likely controlling the observed steady-state composition in the matrix and precipitate average diameter.

1. Introduction

Severe plastic deformation (SPD) is a family of novel methods permitting metallurgists and engineers tailoring the structure and properties of materials [1]. The idea of SPD is to deform the material in a confined space. It permits to increase the strain up to enormous values without fracture of a material. Since a material cannot break, the dynamic equilibrium between deformation-driven production of crystal defects and their relaxation (annihilation) establishes after a certain strain value. It is not astonishing that such a strong action on the material leads to various phase transformations (see Refs. [2–5] and references therein) e.g. the formation or decomposition of a supersaturated solid solution, dissolution of phases, disordering of ordered phases, amorphization of crystalline phases, synthesis of the low-temperature, high-temperature or high-pressure allotropic modifications, and nanocrystallization in the amorphous matrix.

Recently it became clear that the decomposition of (supersaturated) solid solution and dissolution of precipitates during SPD are

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not independent [6]. Moreover, the precipitation of particles of a second phase from a solid solution and their dissolution take place simultaneously and compete with each other. Due to the competition between precipitation and dissolution, a certain steady-state concentration of a second component in a solid solution is reached under SPD. The goal of this paper is to study and understand the mechanisms of this competition, both experimentally and theoretically. The Cu–Ag alloys were chosen for this purpose because all necessary structural, thermodynamic and kinetic constants are known for this well-studied system. The Cu–Ag system has also wide miscibility gap, the absence of intermediate phases and allotropic transformations which facilitates studying decomposition.

2. Experimental

The cylindrical ingots of Cu–3.9 at. % Ag alloy has been prepared by induction melting under vacuum from high purity components (5N Cu and Ag). The melt was poured in vacuum into the water-cooled cylindrical copper crucible of 10 mm diameter. The discs with diameter of $d = 10$ mm and thickness $h = 0.6$ mm have been cut from the as-cast ingots, then ground and etched in a 10% HNO_3 aqueous solution. Some samples placed in sealed and evacuated silica ampoules (residual pressure, $p = 4 \times 10^{-4}$ Pa) have been annealed at $T = 780 \pm 1$ °C during 900 h and then quenched in water at room temperature. At this composition and temperature, the alloy forms a thermodynamically stable solid solution according to the experimental phase diagram [7] (Fig. 1a, full circle). Both types of samples have been deformed by high pressure torsion (HPT) at room temperature during five anvil rotations at the rate of one rotation per minute (rpm) and under pressure, $p = 6$ GPa, in a custom built, computer-controlled device of the Bridgman anvil-type (W. Klement GmbH, Lang, Austria). The anvil with 0.2 mm groove in couple with the flat one were used to get approximately 0.35 mm of the final thickness of the samples. After HPT, the central (low-deformed) part of each disk (about 3 mm in diameter) was excluded from further investigations. Scanning electron microscopy (SEM) investigations have been carried out in a Tescan Vega TS5130 MM microscope equipped with the LINK energy-dispersive X-Ray spectrometer produced by Oxford Instruments. Transmission electron microscopy (TEM) and high resolution TEM (HREM) observations have been made by using an aberration corrected TITAN 80–300 transmission electron microscope with specimens cut from bulk samples at a 3 mm distance from the disc center and further thinned in a FEI Strata 400S dual beam facility. ACOM-TEM technique was used to recognize Cu and Ag phases in the alloys after the HPT deformation. The measurements were carried out on a Philips Tecnai F20ST operated at 200 kV in microprobe STEM mode. NanoMegas ASTAR system was used for ACOM-TEM data acquisition. A probe with about 1 nm diameter and a convergence semi-angle of 1.4 mrad was generated. A camera length of 80 mm was used to acquire the diffraction patterns [8]. X-rays diffraction (XRD) spectra have been collected with a Philips X'Pert powder diffraction apparatus operating in the Bragg–Brentano theta-two theta configuration and the Cu-K_α emission line. Parameters of the XRD peak profiles, such as peak intensity, full width at half maxima and integral breadth, were fitted by Pseudo-Voigt function. A powder LaB_6 standard provided by National Institute of Standards and Technology was used for the correction of instrumental broadening. The mean diameter of precipitates and crystallites (i.e. the size of coherent scattering domains) and micro-strain have been estimated from the broadening of diffraction peaks including reflections up to (420) via a modified Williamson–Hall method [9]. Lattice parameter evaluation was performed by Fityk software [10] using a whole profile refinement. An empirical rule known as Vegard's law was taken into account for subsequent analysis of the decomposition of solid solution or dissolution of precipitates in Cu-rich solid solutions.

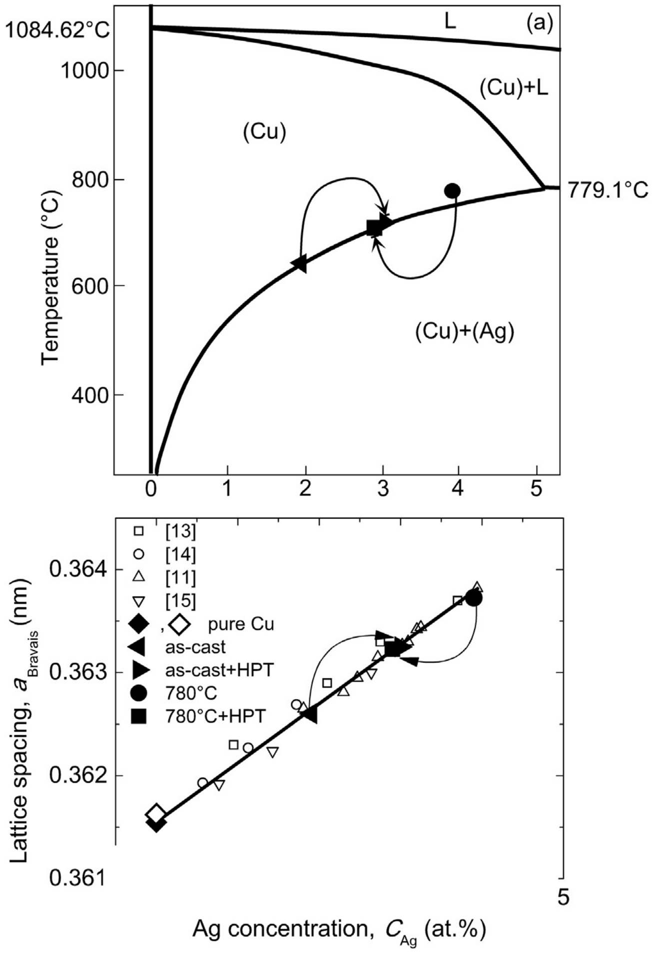

Fig. 1. (a) Cu-rich part of the Cu–Ag phase diagram drawn with data from various sources [7,11,13–15]. The nominal equilibrium composition of the alloy at $T = 780 \pm 1$ °C (full circle) equals the matrix composition of water-quenched samples after long annealing at this temperature (homogenized sample) whereas the full left-triangle marks the matrix content in Ag in the as-cast sample. Matrix compositions after HPT are shown by full right triangle for the as-cast and full square for homogenized samples. They are positioned on the solubility limit in order to show that these could be reached thermodynamically only at temperatures much larger than RT, whereas the arrows connect initial and after-HPT matrix compositions. (b) Bravais lattice constant as a function of Ag concentration in the solid solution. The full line represents the linear least-square fit through data from the literature (open symbols) [11,13–15]. Diamonds represent the lattice spacing in pure Cu: filled diamond at $T = 300$ K before HPT [15] and open diamond after HPT. Other symbols are like in Fig. 1a.

3. Experimental results

3.1. Sample microstructure before HPT

According to the XRD data, the *sample homogenized* at $T = 780 \pm 1$ °C, 900 h and quenched to room temperature (RT) contains the (Cu) solid solution with $c_n = 3.9$ at.% Ag (Fig. 1a, full circle) and vanishing small amount of silver precipitates. The matrix lattice constant determined by XRD is $a \approx 0.36365$ nm. It is close to the a value at $c_n = 3.9$ at.% Ag obtained by linearly interpolating experimental data of lattice spacing as a function of the Ag content in Cu–Ag solid solutions [11–15] (Fig. 1b, full circle). According to the SEM data, the size of (Cu) grains in homogenized