Scripta Materialia 133 (2017) 41–44

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

On the phase evolution and dissolution process in Cu-Cr alloys deformed by high pressure torsion

Jinming Guo, Julian Rosalie, Reinhard Pippan, Zaoli Zhang *

Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, 8700 Leoben, Austria

A R T I C L E I N F O

Article history:
Received 23 December 2016
Received in revised form 4 February 2017
Accepted 6 February 2017
Available online xxxx

Keywords:
High pressure torsion
Cu-Cr nanocrystalline
Dissolution process
Transmission electron microscopy

A B S T R A C T

Normally immiscible 57 wt% Cu–43 wt% Cr compounds were mechanically alloyed by means of high pressure torsion with large and controllable strains. A strain-saturated state in 57 wt% Cu–43 wt% Cr bulk was achieved after 100 rotations deformation (effective strain 1360), with a stable grain size of 13.7 nm and largest solubility of 32 wt% Cu in Cr matrix. The phase fraction change between face-centered cubic and body-centered cubic due to Cu dissolution during continuous deformation was captured and accurately calculated, indicating a negative exponential phase change mode. A phenomenological dissolution mechanism based on the kinetic competition between mixing under sustained external forcing and thermal diffusion induced decomposition was proposed, which was well compliant with the phase evolution observed from experimental results.

Severe plastic deformation (SPD) has drawn an intensive attention for the last two decades due to its superior advantages in developing novel ultra-fine nanocrystalline materials even out of "immiscible" composites [1]. Of the various SPD methods [1], high pressure torsion (HPT) is one of the most efficient mechanical alloying techniques where a disk is subjected to a high applied pressure and concurrent torsional straining [2–5]. For alloys, Cu-Cr was thought one of the promising compounds among non-equilibrium systems in potential applications requiring high strength, good electrical and thermal conductivity, and excellent oxidation and corrosion resistance [6]. The reported results have shown that supersaturated solid solutions of up to 15 at.% (17.7 wt%) Cu in the body-centered cubic (bcc) Cr phase with grain size of 10–20 nm were formed after 25 revolutions of deformation [7, 8]. To date mechanical alloying of Cu-Cr system by either HPT process or ball milling, has found a solubility limit of Cu atoms into Cr of 15 at.%. Such relatively low solubility may limit the further improvement of strength or other properties for bulk materials [7,9].

As already known, alloys generated in so-called "immiscible" systems at room temperature are non-equilibrium, unstable phases. Because even for those systems with liquid miscibility, the thermodynamic driving force for diffusion is dominated by the positive heat of mixing, so that the diffusing atomic fluxes will generally proceed in the direction which causes chemical segregation and phase decomposition. Kinetic models have been proposed to describe the alloying process as a competition between sustained external forcing during plastic deformation and decomposition due to thermal diffusion [10,11]. But up to now, for severely deformed alloys, experiment on the quantitative investigation of phase evolution during deformation hasn't been attempted, and further detailed understanding of the relationship between the extent of dissolution and applied strain is still lacking.

In this work, micrometer-sized staring bulk of nominal 57 wt%–43 wt% Cr (57Cu-43Cr) was deformed with different high-strained revolutions, from 25 rotations to even 1000 rotations in accordance with strain of 340 to 13,600. Simultaneously, phase fractions at different deformation conditions were well calculated and a possible model was proposed based on above-mentioned kinetic model from the phenomenological point of view to describe the dissolution process in details.

The initial bulk material with nominal composition of 57 wt% Cu–43 wt% Cr (volume and atom fraction of about 50%.) was produced by PLANSEE (Reutte, Austria). Disks with a diameter of 8 mm and an initial thickness of about 1.0 mm were HPT-deformed with different numbers of rotations N ($N = 25, 50, 100, 300, 420, 1000$) under a constant pressure of 7.3 GPa and a rotation speed of 0.4 rotation/min. X-ray diffraction (XRD) was conducted on all samples using Smartlab X-Ray Diffractor (Rigaku, Japan) with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540593$ Å). Here it should be emphasized that the X-ray beam width for all the measurements in this work was limited to 2 mm using an incident slit, covering a large area of HPT deformed disk from radius of 2 mm to 4 mm. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) characterizations were carried out using a field emission gun transmission electron microscope (JEOL JEM-2100F, Japan) equipped with an imaging spherical aberration corrector and an Oxford INCA Energy TEM 200 energy-dispersive X-ray spectroscopy (EDXS) system. All microstructural investigations were undertaken at radius of 3.0 mm from the torsional axis of the HPT deformed disks.

---

* Corresponding author.
E-mail address: zaoli.zhang@oeaw.ac.at (Z. Zhang).

http://dx.doi.org/10.1016/j.scriptamat.2017.02.009
1359-6462/

Fig. 1a shows the fine scanning XRD patterns of 57 wt% Cu–43 wt% Cr raw material and deformed samples with different numbers of rotations, and the peaks for $(111)_{\text{fcc}}$ and $(110)_{\text{bcc}}$ are separated from the measured curves (black) by accurate fitting with residual value less than 2%. The final overall fitted curve (red) is nearly the same as measured curve. Fig. 1b shows the relative intensity ratio of $(111)_{\text{fcc}}$ and $(110)_{\text{bcc}}$ calculated based on integrated area of each corresponding peak after subtracting the background [12]. The relative intensity ratio of $(111)_{\text{fcc}}$ decreased obviously from 0.71 for raw bulk material to 0.38 for the sample deformed with 300 rotations. It then remained constant even the sample was deformed further to 1000 rotations. From the relationship between relative intensity ratio and corresponding strain, the relative intensity ratio of $(110)_{\text{bcc}}$ increased quickly when the sample was deformed in the first 100 rotations (equivalent strain $\varepsilon_{\text{eq}} = 1360$), and then this value tended to stabilize at the level around 0.62. Based on the principle that the integrated intensity of diffraction peak for each phase in a mixture is proportional to the volume fraction of that phase [13,14], dissolved Cu content at each strain condition can be obtained by comparing the calculated relative intensity ratio with the values of standard blended Cu-Cr powders of different compositions, which is shown in Fig. 1c. The curve shows an obvious negative exponential change mode, with an approaching value of 32 wt%, indicating the solubility limit of Cu in Cr by HPT is 32 wt%.

Fig. 2a–d show the microstructure characterization of 57Cu-43Cr deformed with 100 rotations. Fig. 2a is a TEM bright field image where grains are equiaxed and randomly distributed, with almost spherical shape. This also facilitates statistic measurement of grain size regarding the grain as a sphere and the diameter of the sphere is the calculated grain size [15]. The inset in top-right corner is grain size statistics histogram with narrow distribution indicating the average grain size is about 13.7 nm, which is based on a statistic measurement of more than 100 grains. Fig. 2b shows HRTEM image of three adjacent grains of Cu and Cr with different zone axes. The grain in right side is Cu with fcc structure and on zone axis of [011] which is parallel to the incident electron beam while the bottom-left grain is chromium with bcc structure and on zone axis of [001]. In this image, $(1\bar{1}0)_{\text{Cr}}$ plane of Cr grain is strictly parallel to $(1\bar{1}1)_{\text{Cu}}$ plane of Cu grain, which is the typical matching relationship of bcc and fcc structure with $\{110\}_{\text{bcc}}//\{111\}_{\text{fcc}}$ [16–18]. In the top-left corner, the grain is not well on zone axis, but $\{111\}_{\text{Cu}}$ planes can still be distinguished from the results of spacing measurement. Fig. 2c shows the high angle annular dark field STEM image, displaying dark areas as Cr grains and bright areas as Cu grains. Fig. 2d shows the weight percentage concentration profile measured across Cu and Cr grains along the white arrowline shown in STEM image Fig. 2c. The spacing between two measurement points for EDXS line-scan is 1.4 nm with an electron probe size of 0.5 nm. EDXS measurement shown here was obtained at the extremely thin area of edge part to insure no overlapping of grains (beam broadening effect is negligible). The concentration profile in Fig. 2d shows that about 30.5 wt% (26.4 at.%) of Cu atoms has been dissolved into Cr grains, simultaneously Cu grains contain about 3.9 wt% (4.7 at.%) Cr dissolved inside.

For the observed negative exponential Cu dissolution in Fig. 1c, here a phenomenological model was proposed to interpret dissolution process based on our experimental data. The idea of thermodynamics-related diffusion was employed to describe the inverse flow of dissolved solute atoms during deformation. Net dissolution flux J is a result of competition between external forcing mixing and thermodynamic back diffusion, equaling to the difference value between external forcing flux J^f and thermodynamic backflow flux J^{th} as shown in Eq. (1):

$$J = J^f - J^{th} \tag{1}$$

In the whole deformation process, the forcing flux J^f is a constant, and the thermodynamic self-diffusion is positively related to the concentration of solute atoms which equals to accumulation of net flux J. Based on this assumption, Eq. (2) can be drawn as follows:

$$dJ^{th} = \kappa\left(J^f - J^{th}\right)d\varepsilon_{\text{eq}} \tag{2}$$

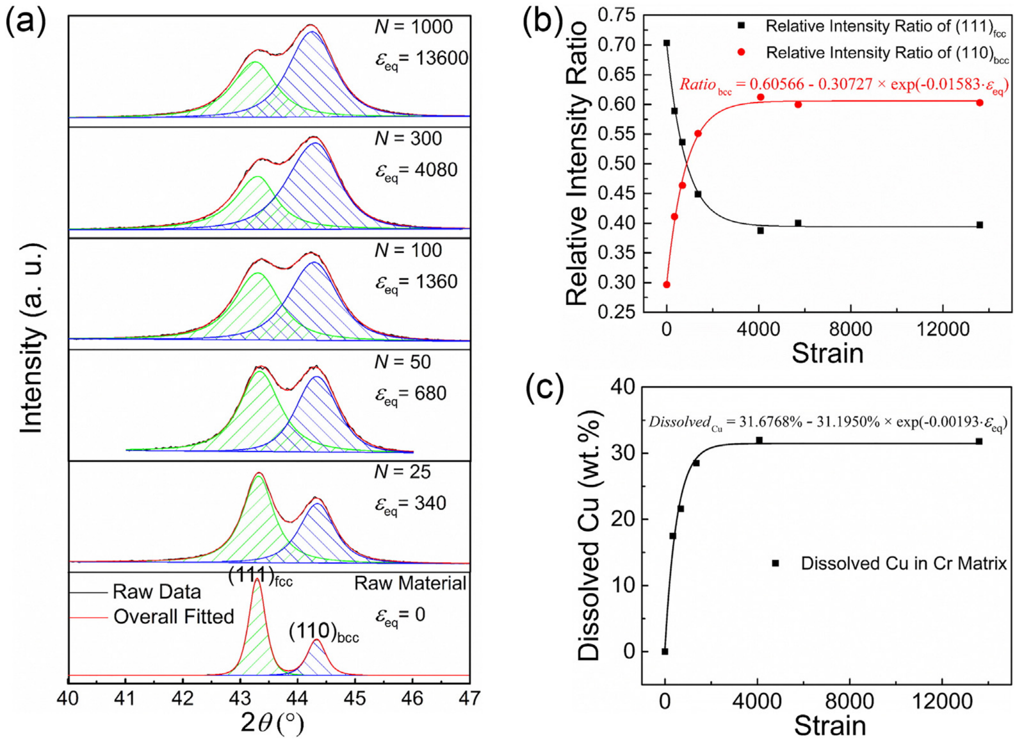

Fig. 1. Phase evolution of HPT deformed samples. (a) XRD patterns of 57 wt% Cu – 43 wt% Cr raw material and as-deformed samples with different numbers of rotations in the range of 40° – 47°. (b) Relative intensity ratio changes of $(111)_{\text{fcc}}$ and $(110)_{\text{bcc}}$ peaks with different numbers of rotations. (c) Dissolved Cu content change as a function of applied strains.