Interfacial diffusion in a nanostructured Cu produced by means of dynamic plastic deformation

H.L. Wang, Z.B. Wang*, K. Lu*

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

Received 9 July 2010; received in revised form 9 September 2010; accepted 21 November 2010
Available online 16 December 2010

Abstract

A nanostructured pure Cu sample consisting of nano-scale twin bundles and nano-sized grains was produced by means of dynamic plastic deformation (DPD) at cryogenic temperature. The apparent activation energy for recrystallization of the nanostructured Cu was determined, being \( \approx 57 \) kJ mol\(^{-1}\). Interfacial diffusion of Zn in the nanostructure was investigated using secondary ion mass spectrometry within the temperature range 358–463 K, in which the volume diffusion is negligible. The measured penetration profiles showed two distinct sections with different slopes, owing to the direct and independent diffusion fluxes along twin boundaries (TB) and grain boundaries (GB). The determined GB diffusivity is \( \approx 2 \) orders of magnitude higher than the TB diffusivity. Relative to the diffusivities and free energies of GB and incoherent TB in coarse-grained Cu, both values in the DPD Cu sample are slightly higher at temperatures <373 K, and approach comparable values at higher temperatures.

*Corresponding authors. Tel.: +86 24 2397 1508; fax: +86 24 2399 8660.
E-mail addresses: zhwang@imr.ac.cn (Z.B. Wang), lu@imr.ac.cn (K. Lu).

Keywords: Nanostructured material; Dynamic plastic deformation; Diffusion; Grain boundaries; Twin boundaries

1. Introduction

Studies of the diffusion behavior of nanostructured materials are not only crucial for understanding their properties and processing, but also provide vital information on the plenty number of interfaces. A large number of diffusion investigations have been carried out on nanostructured and ultrafine-grained (UFG) materials produced by means of severe plastic deformation (SPD) methods [1]. However, the reported results are quite controversial. For example, diffusion studies in an UFG Cu–Zr alloy produced via equal channel angular pressing (ECAP) showed the existence of fast diffusion paths with diffusivity \( \approx 3 \) orders of magnitude higher than that of the relaxed grain boundaries (GB) in the coarse-grained (CG) counterpart [2]. And much enhanced interfacial diffusivities were also detected in some other SPD materials [3–5]. The term “non-equilibrium” GB (i.e., GB with higher excess energies and diffusivities [6]) was proposed for these ultra-fast diffusion paths to distinguish them from conventional GB in well-annealed CG counterparts. However, multiple nanovoids and micropores (or microcracks) were recently detected in ECAP Cu and Cu alloys [7–9], which might form a connected network of open channels and contribute to the ultra-fast penetration of diffusant in UFG samples, especially when a liquid tracer solution was applied as the diffusion source. Meanwhile, consistent GB diffusivities have been observed in materials before and after SPD processing [10–12].

It was noticed that most previous works on diffusion studies of SPD materials were performed on samples prepared by means of ECAP or surface mechanical attrition treatment (SMAT). Besides the detected nanovoids and microcracks, grain sizes in ECAP samples are usually large, being several hundred nanometers for pure metals, and with a high density of lattice dislocations inside the ultrafine grains. These defects influence the measured penetration profiles and the determination of interfacial diffusivities...
By means of SMAT, grains smaller than 100 nm can be achieved in the treated surface layers, but the gradient variation in microstructure along depth creates additional difficulty in clarifying the diffusion behavior of nanostructures [4,14].

Recently, fully dense bulk nanostructured samples of Cu and Cu alloys were synthesized by a newly developed technique, i.e., dynamic plastic deformation (DPD: deformation at high strain rates) [15–17]. In the DPD Cu samples, a large number of nano-scale deformation twins together with nano-sized grains developed from dislocation activities were produced. These samples were expected to provide a unique opportunity for investigating the diffusion behavior of various interfaces and facilitate understanding of the structure and properties of GB and twin boundaries (TB).

Direct measurements of the diffusion properties of TB in conventional polycrystalline metals are difficult, since the diffusion flux along them is usually overlapped by the diffusion fluxes along GB and inside grains. To the authors’ knowledge, TB diffusion was first measured by Minkwitz et al. in a study of the solute diffusion of 195Au in a diffusion-bonded Σ3(1 1 1) Cu bicrystal [18]. It was shown that the diffusion rate along such TB depended on the inclination angle with respect to the symmetrical plane, and it was typically 1–2 orders of magnitude lower than the diffusivity along conventional high-angle GB. Interfacial diffusion behavior was investigated in a nanostructured Cu sample prepared by SMAT, in which grains were formed mainly from the fragmentation of nano-scale deformation twins. The results showed that the measured TB diffusivity in such a microstructure is even close to the GB diffusivity in a well-annealed CG Cu of similar purity, suggesting that the diffusivities along TB and in the nanostructured Cu produced by SPD should be significantly enhanced [4].

In this work, a nanostructured Cu sample with a large number of GB and TB was produced using DPD. The interfacial diffusion behavior of Zn in DPD Cu was investigated at temperatures <463 K. The effect of recrystallization kinetics on interfacial diffusion was studied. The diffusivities along TB and GB, as well as their excess free energies, were determined in terms of the microstructure characteristics and diffusion models.

2. Experimental

2.1. Sample preparation

A cylindrical Cu sample (~99.995 wt.% pure) with diameter 16 mm and height 26 mm was processed by means of DPD at liquid nitrogen temperature (LNT) with a dynamic compression facility [15]. Prior to the treatment, the sample was annealed at 1073 K for 2 h to obtain a homogeneous CG microstructure (with an average grain size of 320 μm; see Fig. 1a). Details of the DPD process can be found elsewhere [15,19]. In the present study, the sample immersed totally in liquid nitrogen was placed on a lower anvil and impacted by an upper anvil. The sample was impacted 18 times, and the overall accumulated strain ε, defined as ln(Lf/L0) was 2.2, where L0 and Lf were the initial and final height, respectively. The strain rate applied to the sample in each impact was estimated to be within 102–103 s–1. No contamination was introduced into the sample during the DPD process. In addition, no cracks or porosities were detected in the prepared samples. Samples for microstructure observations and diffusion measurements were cut from the longitudinal section containing the compression axis in the present study.

2.2. Microstructure characterization

The morphologies of the as-prepared DPD sample and the annealed DPD samples were observed by scanning electron microscopy (SEM), using a FEI Nova-nano microscope equipped with a field emission gun. Detailed microstructures were examined by transmission electron microscopy (TEM), using a JEOL 2010 microscope operated at 200 kV. TEM foils were first cut into slices ~500 μm thick, then mechanically thinned and finally perforated using a twin-jet polisher with a solution consisting of 25 vol.% phosphorus acid, 25 vol.% ethanol and 50 vol.% deionized water at ~268 K.

2.3. Diffusion measurements

In order to exclude the effects of any open channels (if any) on the penetration of diffusant, as in the case of applying a liquid tracer solution [7–9], a Zn layer ~50 nm thick was electroplated as the diffusion source onto the carefully prepared and polished surface of the sample to be measured. An average surface roughness (Ra) of ~8 nm was obtained after the Zn deposition, sufficiently smooth for the diffusion measurements in the present study. Each sample with the deposited Zn was annealed in a glass chamber filled with purified nitrogen in a furnace, of which the temperature was measured and controlled by a thermocouple with an accuracy of ±1 K. The Zn diffusion profiles into the DPD samples after different annealing treatments were determined using secondary ion mass spectrometry (SIMS) on a Cameca IMS 6F analyzer. The primary ion beam used for sputter-sectioning was O2+ (15.0 kV, 400 nA and 0.1 mm in diameter), with a raster area 250 × 250 μm2. The intensities of secondary ions (67Zn+ and 63Cu+) were recorded by a mass spectrometer every 4 s. Generally, the concentration of the analyzed element is proportional to the corresponding measured intensity in SIMS measurements [20]. Therefore, the specific count intensity of 67Zn+ and 63Cu+ in the SIMS crater was used as the concentration in the present study. The sputtering depth was calculated from the sputtering time and the mean sputtering rate, which was determined by the total sputtering time and the total depth of the SIMS crater.

The diffusion parameters and annealing conditions of the DPD sample used in the present work are summarized in
Table 1. At least two different measurements were carried out on each sample to achieve repeatable results for the diffusion profiles. To confirm the accuracy of the present measuring route on the determined diffusivity, a prior experiment was performed on a CG Cu sample, which was deposited on Zn and annealed at 623 K for 120 min. The GB diffusivity was determined as \( \sim 3.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \), consistent with the value \( (5.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}) \) deduced from the reported data [21]. In addition, to check the edge effect of the sputtering crater on the measured SIMS profiles, “zero” profiles were measured with the same sputtering parameters on both the reference DPD and CG samples with electroplated Zn layers prior to diffusion annealing.

3. Results and discussion

3.1. Microstructure observations

Fig. 1b shows the morphology of the as-prepared DPD sample. Intensive plastic deformation is obvious all over the sample, and the coarse equiaxed grains in the original sample (as in Fig. 1a) have been significantly refined. Some lamellar microstructures can be noticed in the DPD sample, with the long axis perpendicular to the impact direction.

Detailed TEM observations revealed that the microstructure of the DPD sample is a mixture of two types of structural features: deformation twin bundles with twin/matrix (T/M) lamellar thicknesses in the nanometer scale and nano-sized grains/cells [15]. As shown in Fig. 2a, a large number of lamellae with an average thickness of \( \sim 50 \text{ nm} \) have been formed, perpendicular to the DPD impact direction. The selected area electron diffraction pattern (SAED; insert in Fig. 2a) shows two sets of \((110)\) diffraction patterns which are symmetrical to each other with respect to the \((111)\) plane. This indicates a twin relationship among the lamellae. A high density of dislocations exists in the T/M lamellae, forming dislocation walls or boundaries. In addition, close observations under high-resolution TEM (HRTEM) revealed that most TB are stepped or curved [15], indicating the presence of a high density of dislocations located within the lamellae and at TB in the DPD sample. The T/M lamellae form bundles with a total width of several hundred nanometers and a length of several to tens of microns.

In addition to the T/M lamellae, numerous grains/cells with sizes ranging from tens to hundreds of nanometers were also observed in the DPD sample. As shown in Fig. 2b, elongated grains with the long axis perpendicular to the impact direction were formed. Typically, the average

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Time (s)</th>
<th>( \sqrt{D_i l (\text{nm})^2} )</th>
<th>( \varphi )</th>
<th>( m )</th>
<th>( D_{TB} ) (m² s⁻¹)</th>
<th>( D_{GB} ) (m² s⁻¹)</th>
<th>( D_{GB}^{(0)} ) (m² s⁻¹)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>D358</td>
<td>358</td>
<td>1.80 \times 10^4</td>
<td>9.0 \times 10^{-6}</td>
<td>1.10</td>
<td>1.95</td>
<td>6.21 \times 10^{-20}</td>
<td>5.93 \times 10^{-18}</td>
<td>5.82 \times 10^{-19}</td>
</tr>
<tr>
<td>D373</td>
<td>373</td>
<td>1.80 \times 10^4</td>
<td>3.3 \times 10^{-5}</td>
<td>1.21</td>
<td>1.89</td>
<td>5.85 \times 10^{-20}</td>
<td>2.51 \times 10^{-17}</td>
<td>2.15 \times 10^{-16}</td>
</tr>
<tr>
<td>D388</td>
<td>388</td>
<td>1.80 \times 10^4</td>
<td>1.1 \times 10^{-4}</td>
<td>1.45</td>
<td>1.79</td>
<td>4.17 \times 10^{-19}</td>
<td>5.82 \times 10^{-18}</td>
<td>7.17 \times 10^{-18}</td>
</tr>
<tr>
<td>D403</td>
<td>403</td>
<td>1.80 \times 10^4</td>
<td>3.3 \times 10^{-4}</td>
<td>1.94</td>
<td>1.64</td>
<td>8.61 \times 10^{-19}</td>
<td>1.13 \times 10^{-17}</td>
<td>2.19 \times 10^{-17}</td>
</tr>
<tr>
<td>D413</td>
<td>413</td>
<td>1.80 \times 10^4</td>
<td>6.5 \times 10^{-4}</td>
<td>2.52</td>
<td>1.51</td>
<td>1.90 \times 10^{-19}</td>
<td>1.62 \times 10^{-16}</td>
<td>4.40 \times 10^{-17}</td>
</tr>
<tr>
<td>D423</td>
<td>423</td>
<td>1.80 \times 10^4</td>
<td>1.3 \times 10^{-3}</td>
<td>3.42</td>
<td>1.36</td>
<td>8.89 \times 10^{-19}</td>
<td>1.45 \times 10^{-16}</td>
<td>8.56 \times 10^{-17}</td>
</tr>
<tr>
<td>D433</td>
<td>433</td>
<td>1.80 \times 10^4</td>
<td>2.4 \times 10^{-3}</td>
<td>4.72</td>
<td>1.22</td>
<td>6.87 \times 10^{-19}</td>
<td>5.63 \times 10^{-16}</td>
<td>1.62 \times 10^{-16}</td>
</tr>
<tr>
<td>D443</td>
<td>443</td>
<td>1.80 \times 10^4</td>
<td>4.3 \times 10^{-3}</td>
<td>6.37</td>
<td>1.11</td>
<td>3.03 \times 10^{-19}</td>
<td>3.92 \times 10^{-17}</td>
<td>2.96 \times 10^{-16}</td>
</tr>
<tr>
<td>D453</td>
<td>453</td>
<td>1.80 \times 10^4</td>
<td>7.6 \times 10^{-3}</td>
<td>8.23</td>
<td>1.04</td>
<td>7.44 \times 10^{-20}</td>
<td>8.69 \times 10^{-17}</td>
<td>5.29 \times 10^{-16}</td>
</tr>
<tr>
<td>D463</td>
<td>463</td>
<td>1.80 \times 10^4</td>
<td>1.3 \times 10^{-2}</td>
<td>10.10</td>
<td>1.01</td>
<td>3.80 \times 10^{-19}</td>
<td>4.73 \times 10^{-17}</td>
<td>9.20 \times 10^{-16}</td>
</tr>
<tr>
<td>Reference</td>
<td>7.20 \times 10^3</td>
<td>5</td>
<td>–</td>
<td>1.00</td>
<td>–</td>
<td>( \sim 3.30 \times 10^{-15} )</td>
<td>5.82 \times 10^{-13}</td>
<td></td>
</tr>
</tbody>
</table>

1. Calculated from the lattice diffusion equation of Cu [27].
2. Calculated from the GB diffusion equation of the CG Cu [21].
The transverse size of these grains is \( \sim 120 \) nm, while the longitudinal size ranges from several hundred nanometers to several micrometers. A high density of dislocations exists in the grains, and the contrast across the boundaries is diffused, resulting from the intensive plastic deformation during the DPD process. Misorientations across these boundaries vary from a few degrees to tens of degrees. It is noticed that no twin relationship is observed among the grains in Fig. 2b by SAED, suggesting that the grains are developed from dislocation activities, i.e., transformed from dislocations cells into subgrains and gradually to randomly oriented refined grains separated by conventional GB [22,23].

TEM observations also showed that some nano-sized grains in the DPD sample were developed from nano-scale T/M lamellae bundles, i.e., the fragmentation of T/M lamellae and the formation of shear bands in the bundles. Detailed microstructure characterization of the LNT-DPD Cu sample and the underlying evolution mechanism can be found in Ref. [15].

Statistical measurements [15] indicated that the LNT-DPD Cu sample is composed of 33% (in volume) of nano-twin bundles with an average T/M lamellar thickness of \( \sim 49 \) nm, 22 vol.% grains evolved from dislocation cells, with an average transverse size of \( \sim 121 \) nm, 30 vol.% of grains fragmented from nano-scale T/M lamellae, with an average transverse size of \( \sim 47 \) nm and an average longitudinal size of \( \sim 120 \) nm, and 15 vol.% of nano-sized grains formed in shear bands, with an average transverse size of \( \sim 75 \) nm and an average longitudinal size of \( \sim 160 \) nm. It is noted that the formation mechanism of nano-sized grains in nano-scale twin bundles was systematically investigated in Ref. [16]. Such a mixture of different microstructures is illustrated schematically in Fig. 2c. Region I denotes nano-twin bundles. Region III denotes the grains fragmented from the T/M lamellae. Grains are separated by TB (or TB-like interfaces, the same hereinafter) along the longitudinal direction in both regions I and III, and by subgrain boundaries along the transverse direction in region III. Region II denotes the other two types of grains, i.e., grains formed by dislocation activities and from shear banding of T/M lamellae. No twin relationship can be found among grains in region II, and they are separated by GB. It should be noted that a large number of dislocations exist both inside the grains and at the interfaces in the DPD sample. The interfaces in the DPD sample are estimated to consist of \( \sim 63\% \) (in area) TB and \( \sim 37\% \) GB.

### 3.2. Recrystallization kinetics

Recrystallization of the deformed structure occurs when the DPD Cu sample was annealed at elevated temperatures. As shown in Fig. 3a, the recrystallized grains are nearly equiaxed and micro-sized (average \( \sim 8 \) µm). Dislocations are seldom observed in them. Statistical observations by SEM show that the recrystallized grains constitute roughly 53 vol.% of the whole sample, while the rest (\( \sim 47 \) vol.%) is still the deformed structure. TEM observations confirmed that the unrecrystallized structure is a mixture of nano-sized grains and nano-scale twin bundles, as discussed in a previous work [24]. The volume fraction of the recrystallized region increases with increasing annealing temperature and duration, following the classic thermal activated nucleation and growth process of static recrystallization.

As shown in Fig. 3b, variations in volume fraction \( f \) of the recrystallized grains with annealing time \( t \) are determined at different annealing temperatures \( T \) within a range 373–463 K. It is clear that \( f \) increases with \( t \) at each temperature, and the recrystallization kinetics are enhanced significantly at higher \( T \). For example, \( f \) reaches \( \sim 58\% \) after annealing at 373 K for 480 min, \( \sim 93\% \) at 403 K for 480 min, and \( \sim 96\% \) at 423 K for 320 min.

The Johnson–Mehl–Avrami–Kolmogrov (JMAK) equation [25] has generally been used to describe the isothermal recrystallization kinetics, i.e.,
where \( n \) is the Avrami exponent and \( k \) is a temperature-dependent parameter following the Arrhenius relationship

\[
k = k_0 \exp \left( -\frac{Q}{RT} \right)
\]  

where \( Q \) is the activation energy for the recrystallization process and \( R \) is the gas constant.

With the measured results of \( f - t \) variations at five different annealing temperatures (Fig. 3b), one can calculate the Avrami exponent \( n \) in terms of the JMAK equation in the following form:

\[
\ln(-\ln(1-f)) = \ln k + n \ln t
\]  

The derived \( n \) and \( \ln k \) values at different temperatures are summarized in Table 2. Usually, it is assumed that \( n \) is temperature-independent within a certain temperature range. Therefore, an average value of \( n = 1.0 \pm 0.2 \) is derived.

With the determined \( \ln k \) values at different annealing temperatures, \( k_0 \) and \( Q \) can be calculated in terms of

\[
\ln k = \ln k_0 - \frac{Q}{RT}
\]  

As shown in Fig. 4, an apparent activation energy \( Q = 57 \pm 4 \text{ kJ mol}^{-1} \) is extracted for the recrystallization process of the DPD Cu within 373–463 K. This value is slightly lower than the activation energy for recrystallization of UFG Cu produced by ECAP (65–96 kJ mol\(^{-1}\)) [26].

The kinetics of static recrystallization of the nanostructured Cu produced by DPD is then described as

\[
f = 1 - \exp \left( -\exp \left[ \frac{57 \pm 4 \text{ kJ mol}^{-1}}{RT} \right] \right) \cdot t^{1.0 \pm 0.2}
\]  

The solid lines in Fig. 3b represent the corresponding fits in terms of the derived JMAK equation at different temperatures, which agree reasonably with the measured data.

**Table 2** Parameters for recrystallization kinetics (as described in Eq. (3)) of the DPD Cu at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>373</th>
<th>403</th>
<th>423</th>
<th>443</th>
<th>463</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>1.19 ± 0.38</td>
<td>0.71 ± 0.08</td>
<td>0.97 ± 0.29</td>
<td>1.10 ± 0.26</td>
<td>1.00 ± 0.15</td>
</tr>
<tr>
<td>( \ln k )</td>
<td>−10.4 ± 0.3</td>
<td>−8.7 ± 0.2</td>
<td>−7.4 ± 0.2</td>
<td>−7.2 ± 0.2</td>
<td>−6.6 ± 0.1</td>
</tr>
</tbody>
</table>
3.3. Diffusion behaviors

3.3.1. Diffusion profiles and effects of microstructure

Fig. 5 shows the measured diffusion profiles of Zn in the DPD Cu samples at different temperatures, in comparison with the profile from the CG sample diffused at 623 K and the “zero” profile. Specific counts of Zn were rescaled for a convenient comparison. As usual, the first several points of each profile close to the surface are disregarded, since they may be associated with the remnant diffusion source, possible contamination or artifacts caused by the stabilization process at the beginning of SIMS sputtering [20]. Concentrations of Zn estimated from the ratio \( I_{Zn}/I_{Cu} + I_{Zn} \) indicate that all the diffusion profiles are measured within the face-centered cubic (fcc) \( \alpha \)-Cu phase region. On “zero” profiles measured on both the DPD sample and the CG sample without any annealing treatment, a sharp decrease in Zn concentration from 100% to the background value within a comparable thickness to the thickness of the deposited Zn layer (~50 nm) was observed (see the “zero” profile in Fig. 5). This suggests that the edge effects of the crater and knock-on effects during sputtering in the present measurements might be negligible.

Taking the Arrhenius temperature dependence of lattice diffusion coefficient \( (D_L) \) of Zn in Cu given by Maruzen [27], one can derive that the lattice diffusion distance is negligible at the temperatures concerned \( (\sqrt{D_L} t \ll 1 \text{ nm}; \text{ see Table 1}) \). Therefore, there is no diffusion from the surface or “short-circuit” diffusion channels into the crystalline bulk, and the penetrations of Zn into the DPD sample are expected to result from diffusion along various boundaries. That is to say, diffusion experiments in the present study are carried out in a Type-C regime according to Harrison’s classification of diffusion kinetics [28]. The classical solution of diffusion equation for one-dimensional diffusion along the x-axis into a semi-infinite body with an instantaneous source can be expressed as

\[
\overline{C}(x, t) = \frac{A}{\sqrt{4\pi D_L t}} \exp\left(-\frac{x^2}{4D_L t}\right) \tag{6}
\]

where \( A \) is a constant related to the quantity of Zn deposited per unit area. It follows that the apparent interface diffusion coefficient \( (D_h) \) can be determined from the experimentally measured diffusion profiles \( \overline{C}(x, t) \) as

\[
D_h = -\frac{1}{4t} \left( \frac{\partial \ln \overline{C}(x, t)}{\partial x^2} \right)^{-1} \tag{7}
\]

However, as shown in Fig. 5, the measured diffusion profiles plotted in the ln \( C - x^2 \) coordinates could not be fitted by a single slope, but they exhibit two distinct sections, i.e., a steep one corresponding to the near-surface region and a shallow one corresponding to the sub-surface region. Although the data on the second section show a larger scatter, the profiles are quite convincing considering the negligible effects of crater edge and mixing during sputtering. It means that different diffusion regimes dominate in these two regions, and diffusion profiles should be analyzed with a more intricate model than with Eqs. (6) and (7). It should be noted that the variation in Zn concentration along depth is not expected to result in such bimodality in diffusion profile (or diffusivity) [29]. In addition, effects of sputtering-induced forward mixing (such as roughness and knock-on effects [30]) are also confirmed to be negligible by the profile measured in the referential CG sample, on which only one branch is detected.

According to the mixed microstructure configuration of the DPD Cu, the overall diffusion profiles \( \overline{C}(x, t) \) can be expressed as

\[
\overline{C}(x, t) = \sum_i \overline{C}_i^h(x, t) \tag{8}
\]

where \( \overline{C}_i^h(x, t) \) and \( \overline{C}_i^h(x, t) \) are the area fraction of various interfaces and the average solute concentration in them, respectively. As confirmed in Ref. [4], the contributions of subgrain boundaries and dislocation walls to the solute...
penetration can be neglected. In addition, the inter-diffusion between GB and TB is insignificant (as clarified later). Therefore, Eq. (8) can be expressed as

\[ \bar{C}(x, t) = \lambda_{TB} \frac{A}{\sqrt{D_{TB}t}} \exp \left( -\frac{x^2}{4D_{TB}t} \right) + \lambda_{GB} \frac{A}{\sqrt{D_{GB}t}} \times \exp \left( -\frac{x^2}{4D_{GB}t} \right) \]  

(9)

here \( \lambda_{TB} \) and \( D_{TB} \) are the area fraction (0.63 vs 0.37) and the diffusion coefficient of TB (GB), respectively. The overall diffusion profiles are determined by the direct and independent C-type diffusion from the surface to the TB region (the first term) and to the GB region (the second term). This aspect will be further confirmed by good agreement between the measured and referential data of diffusivities or interfacial excess energies, as compared later.

According to Eq. (9), it is expected that a significant difference between \( D_{TB} \) and \( D_{GB} \) (e.g., 2 orders of magnitude) will lead to two distinct sections in the diffusion profiles, as shown in Fig. 5. In the sub-surface region with a large depth, the average solute concentration is mainly contributed from the “fast-diffusion” GB while, in the near-surface region, the average solute concentration is contributed from both the GB and the “slow-diffusion” TB. Therefore, in a simple approximation of the independent penetration processes along TB and GB, the diffusivities \( D_{GB} \) and the value of \( A \) can be derived by linearly fitting the sub-surface section in the \( \ln C - x^2 \) coordinates, according to Eq. (7). Subsequently, the average concentration profile contributed from the diffusion along TB (i.e., the TB term) is obtained by subtracting the GB term from the measured profile in the near-surface region according to Eq. (9). \( D_{TB} \) is therefore derived by linearly fitting the obtained TB term in the \( \ln C - x^2 \) coordinates.

Diffusion profiles consisting of two distinct sections with different slopes have also been observed in previous studies, such as in nanostructured Cu produced by SMAT [4,14, in nanostructured \( \gamma \)-FeNi alloy produced by powder metallurgy [31], and in UFG Cu and Cu alloys produced by ECAP [2,7,32]. However, they are associated with different diffusion regimes from the present case. In the SMAT Cu, the appearance of two sections on diffusion profile is attributed to a gradient nanostructure, in which the grain size increases and the dominant interface structure varies with increasing distance from the treated surface, while, in the nanostructured \( \gamma \)-FeNi alloy and UFG Cu and Cu alloys, it results from hierarchical structures of relatively slow and fast short-circuit diffusion paths. In the DPD Cu, no gradient microstructure is found, and the measured diffusion profiles usually exhibit the first (or steep) branch within a penetration depth <0.5 \( \mu \)m, which is much smaller than the characteristic penetration depth of the first branch of the diffusion profile in the hierarchical microstructure case (tens of microns). In fact, while hierarchical microstructures of interfaces might exist in the DPD sample, such as between the nano-twin bundles region and the nano-grains region, their effects on the measured diffusion profiles are insignificant, owing to the relatively small diffusion distance along TB (\( \sqrt{D_{TB}t} \approx 50 \text{ nm} \), as estimated later).

3.3.2. Effects of recrystallization

The above consideration is applicable to the situation with stationary interfaces, i.e., a steady microstructure of grain sizes and interfaces. However, recrystallization accompanies the diffusion annealing processes in the present study, as described earlier. The application of Eq. (9) to penetration profiles measured in such a situation is expected to induce large differences in both the magnitude and the temperature dependence of the apparent diffusion coefficients. This aspect has been introduced into the mathematical treatment of GB diffusion behavior, and diffusivities have been recalculated from the concentration profiles in previous work [10,33].

Unlike the modification done by Glaeser and Evans, who assumed that a steady-state GB migration occurs simultaneously during diffusion and the total area of GB remains constant [33], a model of GB diffusion in recrystallizing materials was proposed recently by Amouyal et al. [10]. This model considered simultaneous recrystallization and type-C diffusion, and enabled quantitative derivation of diffusion parameters from experimentally measured penetration profiles by inputting the explicit JMAK expression for the time-dependence of the volume fraction of the recrystallized region. Since the conditions and assumptions of this model are fulfilled very well by the recrystallization kinetics in the present study, the diffusion behavior in the DPD Cu will be analyzed according to this model hereafter.

As assumed earlier, an apparent JMAK relationship Eq. (5) could be applied to describe the recrystallization processes in both regions of nano-sized grains developed from dislocation activities and twinning. And the overall diffusion profile is expected to be determined by the direct and independent diffusion fluxes from the surface to both regions. Therefore, a full expression of the diffusion profile \( \bar{C} \), which develops in the recrystallizing DPD Cu in terms of parameters \( f \) and \( n \) of the JMAK equation, can be given by

\[ \bar{C} = \lambda_{TB} \frac{A}{\sqrt{D_{TB}t}} X_{TB} \int_{X_{TB}}^{\infty} (2s^2 - 1) \times \exp \left[ -s^2 + \ln(1 - f) \cdot (X_{TB}/s)^{2n} \right] ds \]

\[ + \lambda_{GB} \frac{A}{\sqrt{D_{GB}t}} X_{GB} \int_{X_{GB}}^{\infty} (2s^2 - 1) \times \exp \left[ -s^2 + \ln(1 - f) \cdot (X_{GB}/s)^{2n} \right] ds \]  

(10)

where \( X_{TB} = x/2\sqrt{D_{TB}t} \) and \( X_{GB} = x/2\sqrt{D_{GB}t} \). To develop a simple procedure for the processing of measured penetration profiles, the results of numerical integration of Eq. (10) for arbitrary \( f \) could be fitted with the general expression
where $\varphi$ and $m$ are constants relating to the recrystallization kinetics and are determined by fitting the curves produced by either the TB term or the GB term in Eq. (10) with the respective terms in Eq. (11), $\tau$ is the “effective” diffusion time defined according to the diffusion time $t$ and parameters $k$, $m$ and $n$ [10]. The derived values of $\varphi$ and $m$ are listed in Table 1.

The measured diffusion profiles are re-plotted in the coordinates of $\ln C$ vs $x^m$ with the obtained $m$ values, as shown in Fig. 6. It can be seen that both sections of all the measured penetration profiles are reasonably well linearized. In comparison with the profiles in the $\ln C - x^2$ coordinates (see Fig. 5), it is clear that the recrystallization process significantly affects the diffusion kinetics in the DPD sample, especially at temperatures >403 K, when $m$ values are evidently <2. As discussed previously (i.e., following Eq. (9)), the diffusion coefficients of interfaces $D_B$ could be approximately determined as

$$D_B = \frac{1}{4t} \left( -\frac{1}{\varphi} \frac{\partial \ln C_i}{\partial t} \right)^2$$

That is to say, $D_{GB}$ is derived by linearly fitting the sub-surface section in the $\ln C - x^m$ coordinates directly, and $D_{TB}$ is derived in the near-surface region by linearly fitting the TB term, which is obtained by subtracting the GB term from the measured profile, in the $\ln C - x^m$ coordinates. The TB and GB diffusivities determined are summarized in Table 1 and plotted in Fig. 7.

The solid lines in Fig. 6 represent the corresponding fits by Eq. (11) with the determined $D_{TB}$ and $D_{GB}$ values, i.e.,

$$C(x,t) = \frac{A}{\sqrt{D_{TB}^2}} \exp \left[ -\frac{x}{2\sqrt{D_{TB}^2} \tau} \right]$$

$$+ \frac{A}{\sqrt{D_{GB}^2}} \exp \left[ -\frac{x}{2\sqrt{D_{GB}^2} \tau} \right]$$

Good agreement between the fitting lines and the measured data points supports the validity of the development of diffusion model as described above.

### 3.3.3. Interfacial diffusivities and free energies

As shown in Table 1 and Fig. 7, the values of $D_{TB}$ determined are about 2 orders of magnitude lower than $D_{GB}$ at each measured temperature. This supports the validity of the simplified application of Eq. (12) to determine the diffusivities along GB and TB. Meanwhile, it is noticed that both diffusivities increase with increasing temperature up to 433 K, and then decrease with further increasing temperature. This might be induced by the fast recrystallization kinetics of nanostructured Cu at higher temperatures. The fast recrystallization will result in the formation of isolated “pockets” of unrecrystallized regions surrounded by recrystallized regions, so that the diffusion in such pockets may not contribute to the macroscopic diffusion flux in the following diffusion processes and a decreased apparent diffusivity results [10]. In addition, the possible leakage of impurity atoms from the GB (or TB) into such interfaces as subgrain boundaries and dislocation walls is also expected to decrease the apparent diffusivities at higher temperatures, as discussed by a so-called C-B diffusion regime (i.e., no out-diffusion from interfaces into grains and a significant diffusion from GB to TB) in the SMAT Cu [4]. Therefore, the effective diffusivities determined do not follow the Arrhenius temperature dependence, and no straight lines can be obtained for either $D_{GB}$ or $D_{TB}$ in Fig. 7.

The dependences of lattice and GB diffusion coefficients of Zn in a well-annealed CG Cu on temperature were extrapolated from the Arrhenius relationships given by Refs. [27] and [21], respectively. For comparison, they are also included in Fig. 7. It is clear that both $D_{GB}$ and $D_{TB}$ are much higher than the lattice diffusivity estimated within the temperature range concerned. In comparison with the diffusivity along GB in the CG Cu, the diffusivity along GB in the DPD Cu is $\sim$10 times higher at temperatures <373 K. This is expected to result from a specific state of GB in the DPD Cu [4,6,14]. As discussed previously, the
GB formed via intensive plastic deformation are usually associated with a higher stored energy and/or a higher density of defects compared with the GB in well-annealed CG materials. They may facilitate diffusion by decreasing the vacancy formation energy \[\frac{\Delta G_{\text{v}}}{C_24}\]. The diffusivity along GB in the DPD Cu approaches a value comparable with that in the CG Cu within a temperature range 388–433 K, indicating relaxation of the higher energy state of GB.

Significantly enhanced GB diffusivities have also been demonstrated in several nanostructured (or UFG) materials produced by means of SPD. For example, the diffusivity of Cr in the nanostructured Fe (with grain sizes 10–25 nm) produced by SMAT was 4–5 orders of magnitude higher than that along GB in the CG Fe within a temperature range 573–653 K \[3\], and the diffusivity of Ni along GB in the SMAT Cu was ~4 orders of magnitude higher than that in the CG Cu at 403 K \[4\]. The existence of fast diffusion paths with diffusivity ~3 orders of magnitude higher than that of the relaxed GB in the CG counterpart was also shown in a UFG Cu–Zr alloy produced by ECAP at temperatures 423–623 K \[2\]. In comparison, the GB diffusivity in the DPD Cu is only ~10 times higher than the GB diffusivity in the CG counterpart at temperatures <373 K and becomes comparable at higher temperatures. It means that the GB in the DPD Cu are structurally more relaxed than that in the nanostructured (or UFG) materials produced via other approaches (SMAT or ECAP), owing to the differences in their plastic deformation mechanisms.

There has been so far no reported result on diffusion of Zn along TB in Cu. Diffusivity (or triple product) of Au along TB in a diffusion-bonded \(\sum 3(0 1 1)\) Cu bicrystal was measured to be typically 1–2 orders of magnitude lower than the GB diffusivity in an annealed Cu \[18\]. Diffusivity of Ni along TB or TB-like interfaces in a SMAT Cu was found to be even close to the GB diffusivity in a CG Cu of similar purity \[4\]. In the present work, the diffusivity of Zn along TB is found to be 1–2 orders of magnitude lower than the estimated GB diffusivity in the CG counterpart, suggesting that TB in the DPD Cu should also be more relaxed than TB in the SMAT Cu.

While the vacancy-type diffusion mechanism is well accepted in the lattice of fcc Cu, it is also considered as an approximation in the GB in view of a recent study by molecular dynamics simulations \[35\]. In addition, Zn possesses a similar atomic radius with Cu and can dissolve into it very well (with a maximum solid solubility of \(~38.3\) at.%) \[36\]. Therefore, one may estimate the excess free energy difference of interfaces (GB or TB) \(\Delta\gamma_{\text{TB}}\) in the DPD sample as the difference between the excess free energy of such interfaces \(\gamma_{\text{TB}}\) and the value of referential conventional GB \(\gamma_{\text{GB}}\) in the CG sample following the semi-empirical approach developed in Refs. \[37–39\]

\[
\Delta\gamma_{\text{B}} = \gamma_{\text{B}} - \gamma_{\text{GB}} = \frac{RT}{2aN_0} \ln \frac{D_{\text{B}}}{D_{\text{GB}}}
\]

where \(a\) is the lattice parameter (3.615 Å for Cu), and \(N_0\) is Avogadro’s constant. According to the determined diffusivities of TB and GB (see Table 1) and the diffusivities of conventional GB \(D_{\text{GB}}\) extrapolated from Ref. \[21\], the excess free energy differences of TB and GB in the DPD Cu are obtained at different temperatures <433 K, as shown in Fig. 8. The data at temperatures >433 K are not considered in the present work, since there might be no sufficient reliability in determining the diffusivity due to the effects of fast recrystallization kinetics of nanocrystallites, relaxation of interfaces and the possible change of diffusion regime at higher temperatures (as discussed earlier). For comparison, the excess free energy difference between incoherent TB and conventional GB \(\Delta\gamma_{\text{ITB}}\) ~0.13 J m\(^{-2}\) \[40\] is also shown in Fig. 8. It is clear that the excess free energies of both GB and TB in the DPD Cu sample are slightly higher than the respective referential data at temperatures <373 K, and they approach values comparable with the latter within the temperature range 388–433 K. These correlate with the analyses of temperature-dependences of GB and TB diffusivities, as described before, i.e., interfaces with slightly higher diffusivities and free energies have been produced by DPD, and they relax faster at higher temperatures.

---

\[1\] The validity of this approach in the present system is verified by good agreement between the referential average GB free energy (~0.705 J m\(^{-2}\)) \[40\] and the value estimated (~0.616 J m\(^{-2}\)) by using it from the GB and lattice diffusivities of Zn in a CG Cu \[21,27\], as well as good agreement between the stored energy measured using differential scanning calorimetry (DSC) and the value determined in the present study (as discussed later).
While \( \Delta \gamma \) is estimated as \(-0.705 \text{ J m}^{-2} \) within the concerned temperature range, the free energy of GB is found to be \(0.625 \text{ J m}^{-2} \) at 1198 K and the corresponding temperature coefficient \((-1.0 \times 10^{-4} \text{ J m}^{-2} \text{ K}^{-1})\) reported by Murr [40], the free energy values of GB and TB in the DPD Cu sample are calculated from this value and \( \Delta \gamma \) in Fig. 8. Therefore, the stored enthalpy \( E \) in the DPD Cu could be determined by

\[
E = \frac{1}{\rho} \sum_i A_i^{\gamma_i}
\]

where \( \rho \) is the mass density of Cu \( (8.89 \times 10^3 \text{ kg m}^{-3}) \), \( A_i^{\gamma_i} \) are the density and the free energy of different interfaces (mainly GB and TB), respectively. According to the statistical results in Ref. [15] (also as mentioned in Section 3.1), the densities of TB and GB are estimated to be \(1.3 \times 10^7 \text{ m}^{-1} \) and \(1.0 \times 10^7 \text{ m}^{-1} \), respectively. The stored enthalpy is then derived to be \(1.7 \pm 0.1 \text{ J g}^{-1} \). This value is coincident with the value measured by DSC \((1.7 \text{ J g}^{-1})\) in the DPD Cu with a similar strain [41].

It is noted that the free energy of deformation TB in the DPD Cu is much higher than the free energy of the coherent TB in the as-annealed Cu \((\sim0.037 \text{ J m}^{-2})\) deduced from Ref. [40]. This is expected to be induced by the interaction of a high density of dislocations with TB, as shown by HRTEM observations in Ref. [15]. The free energy of GB varies with the misorientation angle between two adjoining grains and forms a sharp cusp only \(3-4^\circ\) in width around the corresponding angle of the coherent TB, i.e., \(70.5^\circ\) of T/M with \([1 1 0]\) symmetric tilt boundary in Cu [42] and Al [43]. In the DPD Cu, dislocations are accumulated at TB, resulting in a small deviation from the ideal coherent TB misorientations. Therefore, a significant increment of interface free energy is expected to be obtained, while the structure of TB is not disturbed [42].

4. Summary

A mixed microstructure consisting of nano-twin bundles with an average T/M lamellar thickness of \(~50\text{ nm}\) and nano-sized grains/cells was produced in a pure Cu sample using the LNT-DPD technique. Interfaces in this sample are mainly TB (or TB-like interfaces) and GB formed via dislocation activities. Thermal stability investigations show that the apparent recrystallization kinetics of the DPD Cu within the temperature range \(373-463 \text{ K}\) can be expressed as

\[
f = 1 - \exp\left( -\exp\left( \frac{57 \pm 4 \text{ kJ/mol}}{RT} \right) \right) \cdot t^{0.0 \pm 0.2}
\]

Penetration profiles of Zn into the DPD sample measured by SIMS exhibit two distinct sections with different slopes, i.e., a steep one corresponding to the near-surface region and a shallow one to the sub-surface region. Such a bimodality of diffusion profile is expected to be induced by the direct and independent C-type diffusion fluxes along TB and GB. Based on the determined recrystallization kinetics and a model of GB diffusion in recrystallizing materials developed in Ref. [10], the diffusivities of Zn along TB and GB are calculated within the temperature range \(358-463 \text{ K}\).

The GB diffusivity in the DPD Cu is found to be slightly higher than the diffusivity along conventional GB in the CG Cu at temperatures \(<373 \text{ K}\), and is comparable with the latter within \(388-433 \text{ K}\). This might be induced by the relatively higher free energy of GB formed in the DPD process, and they relax to a comparable energy with that of the conventional GB at temperatures \(>373 \text{ K}\).

The diffusivity along TB is \(\sim 2 \text{ orders of magnitude}\) lower than the GB diffusivity in the DPD Cu. In comparison with the free energy of incoherent TB, the free energy of TB calculated from the diffusivity in the present sample is slightly higher at temperatures \(<373 \text{ K}\), and relaxes to a comparable value with increasing temperature. The much higher free energy than that of the coherent TB might be induced by the interaction of a high density of dislocations with TB in the DPD Cu.

In comparison with the nanostructured Cu of a same purity prepared by SMAT [4], both the diffusivities and free energy states of GB and TB are obviously lower in the nanostructured Cu samples processed using the DPD.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Nos. 50621091, 50701044 and 50890171), and the High Technology Research and Development Program of China (No. 2007AA03Z352) are acknowledged. Authors thank Mr X. Si and Prof.
N.R. Tao for sample preparation, and thank Dr S. Divinski and Prof. L.E. Murr for their constructive comments.

References