Materials Science & Engineering A 658 (2016) 296–300

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Dispersion and strength parameter of nano-sized bubbles in copper investigated by means of small-angle X-ray scattering and transmission electron microscopy

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ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form
27 January 2016
Accepted 28 January 2016
Available online 29 January 2016

Keywords:
Bubble dispersion strengthening
Small-angle X-ray scattering
Strength parameter
Size dependence

ABSTRACT

Nano-sized bubble dispersion in copper was achieved by a powder metallurgy method based on ball milling and spark plasma sintering. The microstructure of bubbles was evaluated by using Transmission Electron Microscopy (TEM), and the bubble size and interspacing were further quantitatively determined from small-angle X-ray scattering (SAXS) measurement. From TEM observation, the average radius of bubbles is 2 nm and their interspacing is 75 nm, while according to SAXS measurement, the radius is found to be 1.5 nm and the interspacing is 54 nm. By combining those parameters with the bubble distribution and Vickers hardness, the obstacle strength factor was evaluated as 0.23 by using TEM result, and 0.16 by using SAXS data. This suggested that bubbles could impede dislocation motion.

1. Introduction

Strengthening of alloys due to fine dispersion of oxide particles, void, and helium bubbles induced by irradiation has attracted enormous attention recently [1–3]. MD simulation on dislocation–void interaction has been efficiently studied by Osetsky and Bacon [4,5]. The interaction of dislocations with other cavities caused by irradiation has also been commonly researched [6]. Oono et al. have applied the theory of dislocation–void interaction to the strengthening of bulk materials without irradiation, and succeeded in producing a bubble dispersion in metals by using the pyrolysis gaseous products of polymer PMMA (Poly (methyl methacrylate) during spark plasma sintering (SPS) to probe the strengthening effect of bubbles experimentally [7,8].

The microstructures in the tens-of-nanometre scale, such as oxide particles and bubbles, can be evaluated by using the technology of Transmission Electron Microscopy (TEM). The strengthening effect of bubbles has been discussed by the combination of the microstructure observed by TEM and the increase of Vickers hardness in our past work [7,8]. However, the TEM observation is restricted within small visual field that has micro-scale dimensions and the result is also suffering from the heterogeneous microstructure in the specimen. Structure analyses by using small-angle X-ray scattering (SAXS) can overcome the limitation of TEM method, as it extends the investigation field to more than several tens mm^3 [9,10]. In the present work, the size distribution of bubbles in copper were measured by SAXS, and compared with that observed from TEM. The strength parameter of bubble was obtained by combining these results and the hardness of bubble strengthened copper.

2. Experiments

2.1. Materials

Mixture of copper powder (99.8 mass % and a particle size of 100 μm, by The Nilaco Corporation) and 5 vol% PMMA (Poly (methyl methacrylate) powder was chosen as a starting material. The bubbles dispersion in copper was obtained by using the pyrolysis gaseous products of polymer PMMA. Ball milling was used for the mechanical milling of powder mixture, and subsequent consolidation was accomplished by spark plasma sintering (SPS). The PMMA decomposes at about 600 K [11], and its gaseous products can be used to form bubble dispersion strengthened copper (BDS-Cu). Temperature of 973 K and pressure of 45 MPa were chosen for the SPS process.

2.2. Methods

TEM specimens were fabricated from consolidated BDS-Cu. Slices were cut from the sample and mechanically polished up to a

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http://dx.doi.org/10.1016/j.msea.2016.01.107
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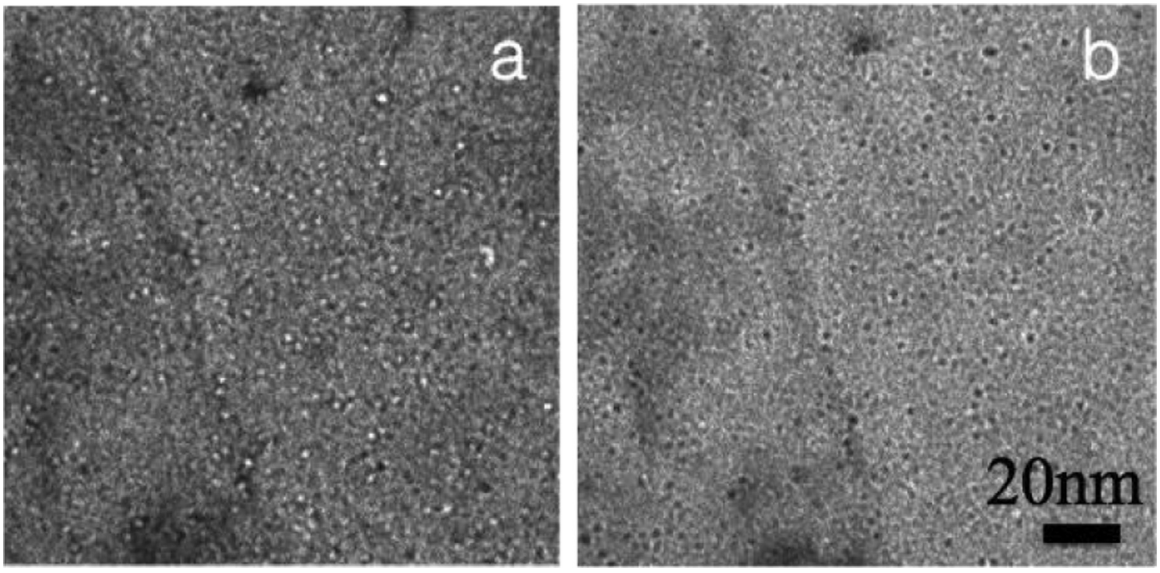

Fig. 1. Characterization of bubble dispersion in bulk copper under TEM : (a) underfocused image; (b) overfocused image.

thickness of 120 μm, from which ϕ 3 mm discs were punched out and thinned to a thickness of 50 μm. The ϕ 3 mm discs were subsequently thinned by Precision Ion Polishing System (PIPS) (Model 691; Gatan Inc) at 113 K with liquid nitrogen as a cooling agent. Microstructural analyses were performed on a JEM-2010 (JEOL Ltd.) operated at 200 kV.

Laboratory SAXS system (Rigaku Nano-Viewer) with Mo-target was used for small-angle X-ray scattering (SAXS) measurement. Two-dimensional confocal mirror tuned for Mo-Ka line and two-dimensional detector (Pilatus 100 K) were installed in this system. The sample was prepared by cutting and mechanical polishing. It has rectangular shape with height and width of 5×4.5 mm and thickness of 0.1 mm. Glassy carbon with 1 mm thick has been used as a secondary standard in SAXS analysis for transforming the results into absolute units [12].

The hardness of the consolidated specimen was tested by using a Vickers hardness tester (HMV-2T: Shimadzu Access Corporation) with a load of 2943 mN for 10 s.

3. Results and discussion

3.1. Characterization by TEM

The TEM images of the synthesized BDS-Cu are shown in Fig. 1. Voids and bubbles with diameter d larger than 5 nm could be imaged by structure factor contrast, while for smaller cavities like void and bubbles with diameter smaller than 1 nm, an out-of-focus imaging may be the only way to be imaged [13]. The through-focus sequence method was applied to obtain the contrast and size distribution of the dispersed bubbles [14]. Bubbles have white regions surrounded by a dark Fresnel fringe in the underfocus images as Fig. 1(a), whereas dark regions surrounded by a bright fringe in the overfocus images as Fig. 1(b). The bubble size was mainly determined from diameter of the inner bright area (corresponding to the inner diameter of first dark Fresnel fringe in the underfocus image, d_{in}) by using a defocus distance $\Delta f = -1$ μm. Fig. 2 presents the size distribution of the bubbles measured by TEM.

The interspacing L of dispersed bubbles can be calculated by using following equation [15]:

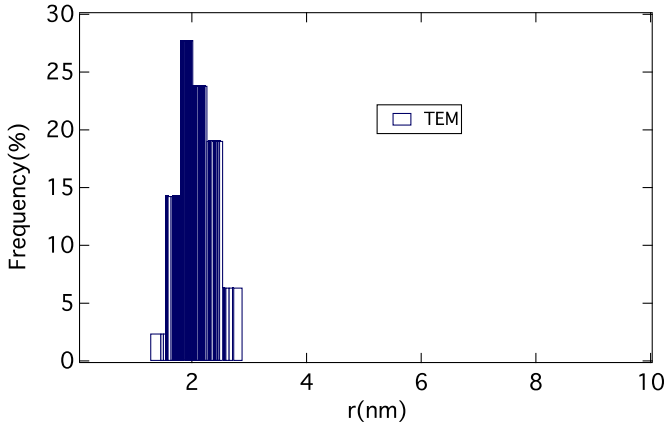

Fig. 2. Size distribution of bubble dispersion in copper from TEM observation.

$$L=\frac{1.25}{\sqrt{2\bar{r}N_v}}-\frac{\pi}{2}\frac{\bar{r}^2}{\bar{r}}=1.25\sqrt{\frac{2\pi\bar{r}^3}{3f\bar{r}}}-\frac{\pi}{2}\frac{\bar{r}^2}{\bar{r}} \quad (1)$$

where the $\bar{r}$, $\bar{r}^2$ and $\bar{r}^3$ are the average, average of square and average of cube of radius, respectively, N_v is the bubble number per volume (volume density) and f is the volume fraction of bubbles dispersed in bulk copper. The 1.25 is the correction factor for the random distribution of bubbles.

In the TEM observation, f was calculated from an area in which most of bubbles have a similar size. And by using the summation of bubble volume, the magnitude of selected area, and the specimen thickness t of that area: $f=\frac{sum(bubble\ volume\ in\ chosen\ area)}{area\ magnitude\times thickness}$ [8]. Since the randomness of bubble distribution has already been considered and reflected as 1.25 in Eq. (1), the main error in determination of f comes from the measurement of specimen thickness and bubble size as well as for the determination of interspacing L. Due to the calculation by Rühle and Wilkens [16] and description of measurement for small bubbles ($2.5\ \text{nm} \le d \le 5\ \text{nm}$) as in Jenkins and Mark's book [13], the measured size d_{in} and has a correlation with true bubble size d_b as $\frac{d_{in}}{d_b}$=110%. The foil thickness was carried out by Convergent–beam Electron Diffraction (CBED) Technique, from which a precise measurement would be give out