Dislocation Density of FCC Metals Processed by ARB

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Abstract
Accumulative roll bonding (ARB) was applied to three FCC metals, such as Al, Cu and Ni. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were made to evaluate dislocation density \( \rho \) of the ARB processed FCC metals. The values of \( \rho \) of ARB processed Cu and Ni increased rapidly after the first ARB cycle, and then, tend to saturate after the following cycles. The evaluated values of \( \rho \) of both ARB 8-cycled Cu and Ni using DSC were around \( 2 \times 10^{15} \) m\(^{-2} \). Whereas, those using XRD were around \( 5 \times 10^{14} \) m\(^{-2} \) (for Cu) and \( 3 \times 10^{14} \) m\(^{-2} \) (for Ni). Although the \( \rho \) values depend on the measurement methods, the trends that DSC values are about an order of magnitude higher than XRD values seem to be common. In the case of Al, dislocation density evaluated using XRD increased to about \( 1 \times 10^{13} \) m\(^{-2} \) at the first ARB cycle, and then gradually decreased to about \( 1 \times 10^{12} \) m\(^{-2} \) with increasing number of ARB cycles.

1. Introduction
Metals having ultrafine grains (UFG), of which grain size less than one micro meter, can be produced by severe plastic deformation (SPD) processes from metals having coarse grains (CG). The strength of UFG metals is several times higher than that of CG counterparts, which is associated with the smaller grain size \( d \) and higher dislocation density \( \rho \) introduced by SPD. Thus, it is important to measure \( d \) and \( \rho \) of UFG.

However, it is relatively difficult to measure \( \rho \) compared with the measurement of \( d \), since the number of applicable measurement methods are limited. In general, all the measurements have their own errors and uncertainties, and therefore, evaluated values rarely coincide. For instance, transmission electron microscopy / scanning transmission electron microscopy (TEM/STEM) can directly observe dislocations, but, there are always some dislocations satisfying the invisible condition and \( \rho \) close to the surface may be reduced due to the image force [1, 2]. Electrical resistivity measurement can detect the change in the amount of lattice defects, but, the contribution of dislocations must be separated from the contribution of grain boundaries and vacancies [3]. X-ray diffraction (XRD) can be also used to evaluate \( \rho \), but, suitable models are requested for the analysis. Differential scanning calorimetry (DSC) can measure the released energy during heating which is stored as lattice defects, but, the contribution of dislocation must be separated from the contribution of the others. Thus, several measurement methods should be adopted for one UFG sample to determine its \( \rho \).

Accumulative roll bonding (ARB) is one of the SPD processes, which can provide plate-shape metals having ultrafine grains (UFGs) [4]. However, \( \rho \) of ARB processed FCC metals are rarely reported using TEM/STEM [1, 2, 5] and electrical resistivity [3]. In the present study, we measured \( \rho \) of three FCC metals; Al, Cu, and Ni, using XRD and DSC in order to determine \( \rho \) as certain as possible.

2. Experimental procedure
The chemical composition of pure Al, Cu, and Ni are shown in Tables 1, 2, and 3, respectively. Al, Cu, and Ni were subjected for the ARB process after annealing at 673K for 7.2 ks,
873K for 7.2 ks, 873K for 3.6 ks, respectively. The initial grain size was about 500 μm for Al, about 30 μm for Cu, and about 20 μm for Ni.

Table 1 Chemical composition of Al.

| Element | Mg | Si  | Fe  | Cu  | Ti  | Zn  | Mn  | Al   |
|---------|----|-----|-----|-----|-----|-----|-----|------|
| mass. % |    | 0.005 | 0.0041 | 0.0001 | 0.0008 | 0.0023 | 0.001 | bal.  |

Table 2 Chemical composition of Cu.

| Element | O  | Ag  | Pb  | Sn  | Fe  | Ni  | Bi  |
|---------|----|-----|-----|-----|-----|-----|-----|
| mass. % | ≤0.002 | ≤0.001 | ≤0.001 | ≤0.001 | ≤0.001 | ≤0.001 | ≤0.001 |
| As      | Sb | Se  | Zn  | Te  | P   | Cd  | Cu  |
| ≤0.001 | ≤0.001 | ≤0.001 | ≤0.001 | 0.002 | ≤0.001 | bal.  |

Table 3 Chemical composition of Ni.

| Element | Co | Fe  | Mn  | Si  | Ni  |
|---------|----|-----|-----|-----|-----|
| mass. % | 0.003 | 0.004 | 0.004 | 0.002 | bal.  |

The ARB process was carried out at room temperature with lubrication up to 8 cycles. The detail of the ARB process can be found elsewhere [4, 6]. A sheet of metal ARB processed with N cycles is denoted as Nc. For instance, a sheet of Ni ARB processed with 8c is expressed as Ni ARB 8c. The annealed sheets before ARB will be denoted as 0c for convenience. The rolling direction, transverse direction, and normal direction are denoted as RD, TD, and ND, respectively. The planes normal to RD, TD, and ND are denoted as RD, TD, and ND planes, respectively.

All ARB sheets with the thickness of 1 mm were cut by a wire arc discharge machine to 5 mm disks for DSC and 10 mm × 10 mm squares for XRD. The damage layer due to arc discharge on the specimens for DSC was removed using acid. The surface of the ND plane of the specimens for XRD was mechanically polished by SiC paper.

DSC measurements were performed using X-DSC7000T (SII nanotechnology) with Al sample holders in Ar atmosphere. The temperature range was between 293 K and 773 K with the heating rate of 5 K/min. The scan was performed twice for each sample in order to check whether a peak can be associated with the stored energy or not. In fact, an exothermic peak was observed only at the first heating process and the entire second scan showed no peaks apart from the peak associated with the magnetic transition.

XRD measurements were performed using SmartLab (Rigaku) with a Cu tube. The parameters for measurements were the applied voltage for the tube of 45 kV, the tube current of 200 mA, the step angle of 0.01 degree, and the scan time of 0.03 s. Bragg peak position and the full width-half maximum, and the wavelength of incident X-ray were used to evaluate lattice micro strain ε with the Williamson-Hall method [7]. In this study, six peaks; (111), (200), (220), (311), (222), and (400), were used. ε was converted to ρ using the following equation proposed by Williamson and Smallman [8].

$$\rho = \frac{16.1\varepsilon^2}{b^2}$$  (1)

Here, b is the magnitude of the Burgers vector.

Grain boundary (GB) maps were constructed using a field emission type scanning electron microscope / electron backscattering diffraction (FE-SEM/EBSD) in JSM7001F (JEOL). The acceleration voltage was 15 kV. Orientation imaging microscopy (OIM) data collection and OIM data analysis (TLS) were used for the measurements and the analysis. The mean grain separation along ND dND, TD dTD and RD dRD were measured using GB maps on TD and RD planes. The shape
of grains was assumed to be rectangular parallelepiped and the grain boundary density \( S_v \) \([m^{-1}]\) is defined as the total area of GB within a unit volume. \( S_v \) was evaluated using the following equation [3].

\[
S_v = \frac{1}{d_{ND}} + \frac{1}{d_{TD}} + \frac{1}{d_{RD}} \tag{2}
\]

In this study, the densities of both total GB \( S_v^{GB} \) and high-angle grain boundary (HAGB) \( S_v^H \) were evaluated using equation 2. Then, the density of low-angle grain boundary (LAGB) \( S_v^L \) was obtained as the subtraction of \( S_v^{H} \) from \( S_v^{GB} \). Here, GB having the misorientation angle less than 15° is defined as LAGB, whereas, GB having the misorientation angle more than 15° is defined as HAGB.

3. Results and discussions

Figure 1 (a)-(c) show DSC curves for Al, Cu, and Ni ARB1c-8c, respectively. These curves were from the first scan, and there were no peaks for the second scan. Because, these first peaks are associated with released-stored energy. The broad peaks were measured for most of specimens apart from Al ARB1c-2c. Here, a small spike at around 631 K in each Ni curve is due to the magnetic transition.

For Al, ARB1c and ARB 2c show no specific peaks. Though some humps in the DSC curves start to appear with increasing \( N \), they are still near the lower detection limit of the DSC apparatus. ARB processed Al with 7c-8c show characteristic three broad peaks. For Cu and Ni, only one peak was observed at each specimen, and, the peak height seems to increase with increasing \( N \). The peak temperature \( T_p \) defined as the centre value of temperature for the peaks decreases with increasing \( N \) for all the ARB specimens.

Figure 1 (d) shows \( N \) dependence of released-stored energy density \( E_s \) measured by estimating the area under the peak of the DSC curves for Al, Cu, and Ni. Since well annealed specimens were used as a reference for DSC, \( E_s \) of ARB 0c for Al, Cu, and Ni are assumed to be zero. Thus, strictly speaking, the released \( E_s \) is defined as increase in the stored energy from that of ARB 0c specimens.

For Al, \( E_s \) remains zero up to ARB 2c since there are no peaks on DSC curves. \( E_s \) of ARB Al increases from zero to around 1 MJm\(^{-3}\) with increasing \( N \) to seven. After ARB Al 7c, \( E_s \) saturates at about 1 MJm\(^{-3}\). For Cu, \( E_s \) increases from zero to around 8 MJm\(^{-3}\) with increasing \( N \). For Ni, \( E_s \) increases from zero to around 9.5 MJm\(^{-3}\) with increasing \( N \) up to five, and then, \( E_s \) seems to saturate.

Three types of lattice defects; GBs, dislocations, and vacancies, can contribute to \( \gamma_i \) [9-13]. Thus, it is necessary to separate each contribution in order to evaluate \( \rho_i \).

Let us first consider the contribution of GB. The GB energy density \( E_{GB} \) can be written as follows [13].

\[
E_{GB} = S_v \gamma \tag{3}
\]

Here, \( \gamma \) is the energy density of GB [Jm\(^{-2}\)]. We now consider that \( \gamma \) is a function of misorientation angle \( \theta \) of the two abutting grains and is written as [14, 15],

\[
\gamma_0 = \begin{cases} 
\gamma^H \left( \frac{\theta}{15} \right) \left[ 1 - \ln \left( \frac{\theta}{15} \right) \right] & : \theta \leq 15^\circ \\
\gamma^H & : \theta > 15^\circ 
\end{cases} \tag{4}
\]

Here, average \( \gamma \) for HAGB \( \gamma^H \) is 0.32 Jm\(^{-2}\), 0.64 Jm\(^{-2}\), and 0.87 Jm\(^{-2}\) for, Al Cu, and Ni, respectively [16]. In this study, EBSD was used to evaluate \( S_v \) so that GB having misorientation
angle $\theta$ less than $2^\circ$ could not be detected. The average $\gamma$ for LAGB $\gamma^L$ was evaluated from the misorientation distribution chart constructed from the EBSD data.

Thus, it is necessary to evaluate $S^V_L$ and $S^H_V$ in order to evaluate $E_{GB}$. Figure 2 (a)-(c) shows $N$ dependence on $S^L_V$ and $S^H_V$ for Al, Cu, and Ni, respectively. The $S^L_V$ of ARB0c for all metals is nearly zero since there are almost no LAGBs on GB maps. For Al ARB1c and Cu ARB1c, there are too many LAGBs on GB maps so that $S^L_V$ was impossible to evaluate. However, $S^H_V$ is expected to be in the order of $\text{Mm}^{-1}$ since $S^H_V$ of other specimens is between $2 \text{ Mm}^{-1}$ and $5 \text{ Mm}^{-1}$.

Since $S^{GB}_V$ and $S^H_V$ are now known for all the ARB specimens, it is possible to estimate $E_{GB}$ from equation 5. Figure 3 shows the measured $E_s$ and estimated $E_{GB}$. For most Cu and Ni specimens, $E_s$ is larger than $E_{GB}$ so that the difference between $E_s$ and $E_{GB}$ is expressed as white bars in Fig. 3.

On the other hand, $E_s$ and estimated $E_{GB}$ are comparable for Al and both are rather small. Thus, it is concluded that measured $E_s$ mainly comes from $E_{GB}$ for Al, and the other contributions such as by dislocations and vacancies must be small.

Secondly, the contribution of vacancies for $E_s$ will be considered. This contribution $E_{\text{vac}}$ is expressed as follows.
Here, \( e_{\text{vac}}, C_v, N_A, \) and \( V_M \) are the formation energy of a vacancy, vacancy concentration, Avogadro's number, and molar volume, respectively. Even a situation well above recrystallization temperature is considered, \( E_{\text{vac}} \) is much less than measured \( E_s \) for Cu and Ni. Thus, \( E_{\text{vac}} \) is assumed to be zero in this study. Furthermore, there is a report that \( E_{\text{vac}} \) is negligible compared with the measured \( E_s \) of rolled pure metals [13]. This is also supported by electrical resistivity measurements indicating that \( C_v \) is almost constant before and after the ARB process [3].

\[
E_{\text{vac}} = e_{\text{vac}}C_vN_A/V_M 
\]  

(6)

Figure 2 Density of GB versus ARB cycle number for (a) Al, (b) Cu, and (c) Ni.

Figure 3 Estimated stored energy density with considering the contribution of LAGB and HAGB for (a) Al, (b) Cu, and (c) Ni.

Thirdly, the contribution of dislocations \( E_{\text{disl}} \) has to be considered. The evaluation of \( \rho \) from \( E_{\text{disl}} \) is one of the purposes of this study. \( E_{\text{disl}} \) is expressed as equation 7, with considering the elastic strain energy of dislocation per unit length and \( \rho \).

\[
E_{\text{disl}} = a\mu b^2 \rho
\]  

(7)

Here, \( a \) is the coefficient with the value of about 0.5 and \( \mu \) is the shear modulus. \( \mu = 79 \) GPa and \( b = 0.249 \) nm are used for Ni, and, \( \mu = 48 \) GPa and \( b = 0.256 \) nm are used for Cu. By assuming \( a = 0.5 \), we can estimate \( \rho \) from equation 7.

Figure 4 shows \( N \) dependence of the increment of dislocation density \( \delta \rho \) from ARB 0c for Cu and Ni. \( \delta \rho \) for both Cu and Ni increase from zero m\(^2\) to \( 2 \times 10^{15} \) m\(^2\) with increasing \( N \) from zero to two, and then, saturate. This trend agrees with the reported change in \( \rho \) for 2N-Al with ARB process.
measured by TEM/STEM [2]. It should be noted that $\rho$ of annealed pure metals are normally about $10^{11}$–$10^{13}$ m$^{-2}$. Thus, when $\delta\rho$ is more than $10^{14}$ m$^{-2}$, $\delta\rho$ can be regarded as $\rho$ for all practical purposes.

![Increment of dislocation density](image)

**Figure 4** ARB cycle number dependence on increment of dislocation density evaluated using DSC.

Figure 5 shows $N$ dependence of $\rho$ for Al, Cu, and Ni evaluated using XRD peak broadening. All ARB 0c specimens have small $\rho$ compared with their ARB processed specimens. For Al, $\rho$ rapidly increases at $N = 1$, and then gradually decreases with increasing $N$. For Cu and Ni, $\rho$ significantly increases at the first ARB cycle, and then remains similar as values.

![Dislocation density](image)

**Figure 5** Dislocation density evaluated using XRD peak broadening.

The saturation values of $\rho$ for Cu and Ni ARB1c-8c is about one order of magnitude different between XRD and DSC. Thus, it is important to know that there are uncertainties for the measurements of $\rho$.

### 4. Conclusions

Evaluation of dislocation density of ARB processed FCC pure metals; Al, Cu, and Ni, were performed using DSC and XRD. Stored energy was measured using DSC, and then, the contribution of GB for stored energy was subtracted. Although the stored energy of Al could be explained as being composed of GB energy, that of Cu and Ni contains other contributions. The difference of the energy between the measured stored energy and the contribution of the GB energy was identified to be due to the accumulation of dislocations. The dislocation density of Cu and Ni was evaluated. Peak broadening of XRD was also converted to dislocation density of Al, Cu, and Ni. As a result, it was found that dislocation density significantly increased after the first cycle of ARB for all metals. Then, dislocation density of Al slightly decreased with increasing the ARB cycle number whereas,
dislocation density saturated for Cu and Ni. The saturated value evaluated from DSC was about $2 \times 10^{15}$ m$^{-2}$ for both Cu and Ni. In the case of Al, dislocation density evaluated from XRD decreased from around $1 \times 10^{13}$ m$^{-2}$ to around $1 \times 10^{12}$ m$^{-2}$ with increasing the ARB cycle number from one to eight. The saturated value evaluated from XRD for Cu was about $5 \times 10^{14}$ m$^{-2}$, and that for Ni was about $3 \times 10^{14}$ m$^{-2}$.

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References
[1] Miyajima Y et al 2013 Acta Mater. 61 1537-1544
[2] Miyajima Y et al 2010 Mater. Sci. Eng. A 528 776-779
[3] Miyajima Y et al 2010 Philos. Mag. 90 4475-4488
[4] Azushima A et al 2008 CIRP Annu.-Manuf. Technol. 57 716-735
[5] Kamikawa N et al 2009 Acta Mater. 57 4198-4208
[6] Saito Y et al 1999 Acta Mater. 47 579-583
[7] Williamson G K and Smallman R E 1955 P. Phys. Soc. Lond. B 68 577-585
[8] Williamson G K and Smallman R E 1956 Philos. Mag. 1 34-46
[9] Zhang Y et al 2008 J. Mater. Sci. 43 7326-7330
[10] Takata N et al 2007 Mater. Trans. 48 2043-2048
[11] Cao W Q et al 2008 Mater. Sci. Eng. A 492 74-79
[12] Rohatgi A and Vecchio K S 2002 Mater. Sci. Eng. A 328 256-266
[13] Knudsen T et al 2008 Metall. Mater. Trans. A 39A 430-440
[14] Godfrey A et al 2005 Metall. Mater. Trans. A 36A 2371-2378
[15] Zhilyaev A P et al 2005 Mater. Sci. Eng. A 391 377-389
[16] Murr L E 1975 Interfacial Phenomena in Metals and Alloys (London, Addison-Wesley)