Change in Microstructure and Electrical Resistivity of Cu–Zn Alloy Due to Rolling

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In order to reveal the change in electrical resistivity and strengthening due to plastic deformation and microstructural evolution, investigation of mechanical and electrical properties was performed. From microstructural observations, it was found that the heterogeneous-nano structure having “eye”-shaped twin domains was formed of which volume fraction becomes largest at 90% of rolling reduction. Ultimate tensile strength increases with increasing rolling reduction and reaches about 735 MPa at 90% and 95% reductions. The electrical resistivity measured at 77 K changes from about 39.6 Ωm to about 61.9 Ωm, and correspondingly, the conductivity at 293 K changed from about 28.0 IACS down to about 19.9 IACS. When comparing the total changes in electrical resistivity before and after reduction of 80%, the latter was larger. The more obvious changes in mechanical and electrical properties over reduction of 80% are associated with the formation of heterogeneous-nano structure in addition to increasing dislocation density. [doi:10.2320/matertrans.MT-D2021005]

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1. Introduction

Cu–Zn alloys, also called Brass, have been widely used since the ancient times due to their relatively high strength, ductility, and formability. As the main application, they were often used as wires for arc discharge wire cutting machines and electrically conductive materials for electronic parts, in addition to water supply pipes and wind instruments. Although they were used as electrically conductive materials, there were few systematic reports about their change in electrical properties caused by plastic deformation and measured temperatures.1)

Free electrons in metals averagely move towards the opposite direction of the current direction while scatterings. Here, the mean distance that the free electrons can move straightly without scatterings is called the mean free path, and the lower mean free path results in the higher electrical resistivity (nΩm).2) Of course, electrical conductivity becomes lower when the mean free path becomes lower. As scattering centers, the lattice vibration and the impurity atoms are well known. Besides them, lattice defects such as vacancies, dislocations, and grain boundaries can be the scattering centers of electrons.3, 4) It is always required to develop conductive-metallic materials having higher strength with maintaining their conductivity, and it is not the exception for Cu–Zn alloys. Thus, the relationships between mechanical and electrical properties and microstructure were studied in order to reveal the strengthening and change in the electrical resistivity of Cu–Zn alloy due to plastic deformation.

Table 1 Chemical composition (mass%) of provided Cu–Zn alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Fe</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>68.89</td>
<td>0.001</td>
<td>0.002</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2. Experimental Procedures

2.1 Sample preparation

Cu–30%Zn alloy (JIS number C2600) with a diameter of 14.8 mm was subjected to this study. The chemical composition of provided Cu–Zn alloy is shown in Table 1. Judging from the phase diagram,8) the Cu–Zn alloy used in the present study is a single phase. The bar-shaped provided material was mechanically cut to a rectangular shape with 4 mm thick × 14.8 mm width × 122 mm length, then annealed at 873 K for 7.2 ks in ambient condition using a furnace (KBF828n1, Koyo), and then used as a starting material. The starting material was cold-rolled using a rolling mill (Japan Cross Atuen) with the rolling reduction between 0% and 95%, and each specimen was cut to be a length of about 52 mm. Here rolling reduction of 0% means the specimen without rolling, and the initial grain size was 77 µm. As the sample coordinates, three directions: rolling direction (RD), transverse direction (TD), and normal direction (ND), were defined. Hereafter, the planes perpendicular to RD, TD, and ND were called RD, TD, and ND planes. Since the specimens with the rolling reduction of 20% and 40% were not perfectly flat sheets and slightly bent, the surface was mechanically polished by emery papers and strait sheets were prepared. Specimens for observations/measurements were also cut by an arc discharge-wire-cutting machine (HS-300, Brother) from the prepared sheets.

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2.2 Tensile tests

Tensile tests were performed on the specimens cold-rolled to various rolling reductions using an Instron type tensile machine (AG-X 10N-10kN, Shimadzu). Test conditions were the crosshead speed of 10 mm/min, at room temperature and in ambient atmosphere. The shape of specimens was shown in Fig. 1, and the gauge length was 10 mm and gauge width was 3 mm. The thickness of each tensile specimen was the thickness of the rolled sheet. The rolled sheets having more than 1 mm-thickness were reduced to 1 mm using an arc-discharge-wire-cutting machine and mechanical polishing.

2.3 Electrical resistivity measurements

Using a four-terminal method at room temperature (293 K) and liquid nitrogen temperature (77 K), electrical resistivity, \( R \), of each specimen having different rolling reduction was obtained. Here the constant current of 10 mA was passed, and the electrical resistivity measurements using the four terminal-method can be found elsewhere.\(^4,5\) In this study, a precise current source 6220 (Keithley) and a nanovoltmeter 2182 (Keithley) were used. Cu wires with a diameter of 0.3 mm (Nilaco) were spot-welded with the specimen using a spot welder NRW-100A and a head NA-60A (Nippon avionics). In order to avoid the delamination of welded spots between the specimen and the Cu wires due to handling, an ABS resin frame 3D-printed using a 3D printer (da Vinci 1.0, XYZ printing) was used. The ARB resin frame could be fabricated much easier than that made by quartz glass (Fig. 2).

Concerning to the size of the specimens for electrical resistivity measurements, the thickness and the width were measured by a digital micrometer, and the distance between two wires for measuring voltage drop was measured by a digital caliper. Using the cross-sectional area, \( s \) (m\(^2\)), and the distance between the two wires, \( l \) (m), the electrical resistivity, \( \rho \), was evaluated using the following equation.

\[
\rho = \frac{R \cdot s}{l}
\]  

The specimens for electrical resistivity measurements were cut from the rolled sheets using the arc-discharge-wire-cutting machine as the RD becomes the longitudinal direction. The length and width of the specimens were 45 mm and 1 mm, respectively. The surface of the specimens was mechanically polished by #2000 emery paper.

2.4 Microstructure observations

The TD plane of the sheets having different rolling reductions was observed using a field emission-scanning electron microscope (FE-SEM, JSM-7001F, JEOL), and backscattered electron images (BEIs) were obtained. Also, electron backscatter diffraction (EBSD) analyses were performed in the FE-SEM. Specimens for the observation were cut using the arc electric discharge cutting machine to have a size of TD 1 mm × RD 3 mm with the rolling reduction down to 60%, and TD 2 mm × RD 3 mm for that equal to and more than 80%. The observation plane was mechanically polished by #2000 emery paper and then electrolytically polished to have the mirror-like surface in 33% nitric acid:methanol = 1:2 in volume) at 243 K with the applied voltage of 14.75 V for 75 s.

The EBSD measurements were performed in the FE-SEM, with the acceleration voltage of 15 kV, using OIM Data Collection ver. 7 (TSL), and the step size was 0.05 μm. The analysis of the EBSD was carried out using OIM Date Analysis, and grain boundary (GB) maps were constructed from EBSD data. The GBs with a misorientation less than 15° were displayed using red lines as low-angle grain boundary (LAGB), and the GBs with equal and more than 15° were indicated by the green lines as high angle grain boundary (HAGB). The GBs with a misorientation of less than 2° were omitted for the analyses due to the limitation of the measurement accuracy.

2.5 X-ray diffraction

To determine dislocation density \( L_V \), X-ray diffraction (XRD) measurements were performed on the ND plane of each sheet having different rolling reductions. Each specimen was cut to be TD 10 mm × RD 10 mm, and the surface was mechanically polished by #2000 emery paper until the 1/4 of the initial thickness was removed. An X’pert PRO MPD (PANAlytical) was used for the XRD measurements. Applied conditions for the measurements were the tube voltage of 45 kV, tube current of 40 mA, wavelength \( \lambda = 0.15418 \text{nm} \) (Cu-Kα line), range between 38° and 150°, and the step size of 0.0334°.

Using full width-half maximum (FWHM) of the measured peaks, the value of lattice strain was evaluated based on the Williamson–Hall method.\(^9,10\) Here, an analysis software Fityk 0.8.6 was used for the curve fitting to determine FWHMs of the diffraction peaks. The obtained lattice strain was converted to \( L_V \) using following eq. (2).\(^11\)
Here, $K$ is a constant depending on the crystal structure and 16.1 for fcc, $e$ is the lattice strain, and $b$ is the magnitude of the Burgers vector (0.256 nm).

3. Experimental Results and Discussion

3.1 Microstructure observations

Figure 3 shows SEM/BEIs taken with the magnification of $\times 2000$. It can be seen in Fig. 3(a) that the dislocation substructure was introduced by the rolling in the specimen cold-rolled to 40%. In the 60%-specimen, as shown in Fig. 3(b), lamellae elongated to the RD and shear bands are already developed in a portion of the specimen. The lamellar structure was fully developed in almost all the areas observed in the 80%-specimen (Fig. 3(c)). It should be noticed that a different microstructure with the rhombus shape can be seen in Fig. 3(c). Sharp liner contrasts parallel to RD were detected only in the rhombus regions. When the rolling reduction reached 90%, above mentioned rhombus-shaped microstructures were divided, and fragmented to be smaller rhombus-shaped regions. The small rhombus regions seem to be dispersedly embedded in the lamellar microstructure (Fig. 3(d)). They are typical “eye-shaped” twin domains surrounded by shear bands found in the heterogeneous-nano structure formed by the heavily cold rolling of metals and alloys with low stacking fault energy (SFE). With increasing the rolling reduction up to 95%, the rhombus-shaped regions become smaller, and the area fraction also becomes smaller (Fig. 3(e)).

In Figs. 4(a)–(c), higher magnified BEIs of the specimens cold-rolled to 80%, 90%, and 95% are shown. These images make it possible to distinguish between the elongated lamellar microstructure often observed in severely cold-rolled materials and the rhombus-shaped regions. Thin regions consisting of smaller and equiaxed grains can be seen at the boundaries between the lamellae and rhombus-shaped regions. Furthermore, the clear liner contrasts parallel to RD exist in the rhombus-shaped region, which are reported as twin boundaries. Microstructure observations with the higher magnification confirm the rhombus-shaped regions in the 80%- and 90%-specimens as shown in Fig. 4(a) and (b), but both the size and the area fraction of rhombus-shaped regions of the 95%-specimen become smaller (Fig. 4(c)). It can be thought that the shear banding fragmented the rhombus regions and that the part of the regions was transformed into lamellar microstructure.

Figure 5 shows the GB maps of specimens cold-rolled to 40%–95%. It is still possible to distinguish HAGBs represented as green lines and LAGBs represented as red ones even in specimens cold-rolled to over 60%, in which

![Fig. 3 BEI images of Cu-Zn alloys with different rolling reductions of (a) 40%, (b) 60%, (c) 80%, (d) 90% and (e) 95%.](image-url)

![Fig. 4 Magnified BEI images of Cu-Zn alloys with different rolling reductions of (a) 80%, (b) 90% and (c) 95%.](image-url)

![Fig. 5 Grain-boundary (GB) maps of Cu-Zn alloys with different rolling reductions of (a) 40%, (b) 60%, (c) 80%, (d) 90% and (e) 95% described by green and red lines which indicate high-angle and low angle grain boundaries.](image-url)
grain refinement proceeded, though the number of the unindexed points indicated by the black dots increases. Although they are not an identical area, with comparing BEI and GB map, both HAGB and LAGB are rarely detected in the 40%-specimen (Fig. 5(a)), and the linear contrasts within grains seen in the BEI should be dislocation walls formed during the development of the dislocation sub-microstructure. In the specimen cold-rolled to 60%, lamellae elongated along RD are formed at some regions, as shown in Fig. 5(b). The fraction of HAGBs represented as green lines, including twin boundaries, is high in this regions. Although the lamellar ultrafine grains are elongated along RD, it can also be recognized that the grains were divided into some parts by GBs parallel to ND. By contrast, only LAGBs indicated by the red lines were only visible within a grain occupying the right 1/4 of Fig. 5(b). Therefore, it can be understood that the grain refinement was retarded in the area (the right side of Fig. 5(b)) compared with the other area (the left side). The coexistence of the regions with and without grain refinement is probably due to the variation in initial grain orientation. Some grains have more favorable crystallographical orientations for mechanical twinning, and as a result, grain refinements are more likely to proceed. On the other hand, grain refinement is less likely to occur in grains where mechanical twinning is less likely to occur. When the rolling reduction reaches 80% and 90%, the microstructure mainly consisted of the rhombus and the other regions (Fig. 5(c) and (d)). With the comparison of the BEIs, the many unindexed points in the GB maps are concentrated within shear bands. Also, the increase of the unindexed points are attributed to the increase of the internal strain and the progress of the grain refinements. Moreover, it was pointed out that the linear contrasts parallel to RD within the rhombus regions are the HAGBs, i.e., deformation twins.14,16 Although the GB map of the 95%-specimen (Fig. 5(e)) contains a considerably high amount of unindexed points compared with the other rolling reduction, both the size and the area fraction of rhombus regions seem smaller.

Microstructure containing the rhombus regions was reported in the heavily cold-rolled Cu–Be system alloy and SUS316LN austenite stainless steel.12–16 The rhombus regions are also called “eye-shaped” microstructure based on transmission electron microscopy with higher resolution than SEM. The eye-shaped regions are twin domains composed of ultrafine twin bands, and the matrix consists of ultrafine lamellar microstructure. These two structures are divided by shear bands consisting of equiaxial ultrafine grains. Above mentioned complicated microstructure consisting of deformation-induced microstructure is called heterogeneous-nano structure. The heterogeneous-nano structure is developed when fcc metals with low stacking faults energy (SFE) are subjected to heavy cold rolling, leading to high strength and high ductility.14 Since the SFE of the Cu–Zn alloy used in the present study is lower than pure Cu by the Zn addition, widely extended stacking faults should suppress the motion of dislocations, resulting in more significant work hardening, which easily causes twin deformations. The relatively low SFE of the present alloy should lead to the development of the heterogeneous-nano structure.

Figure 6 shows the rolling reduction dependence of dislocation density evaluated using Williamson-Hall method. The dislocation density increases around $2.2 \times 10^{15}$ m$^{-2}$ from around $3.0 \times 10^{14}$ m$^{-2}$ to around $2.5 \times 10^{15}$ m$^{-2}$ with increases in the rolling reduction.

### 3.2 Change in mechanical properties

Figure 7 shows stress-strain curves evaluated from tensile tests of Cu–Zn alloy specimens cold-rolled to various reductions of 0%–95%. Compared with the annealed specimen (0%), the ultimate tensile strength (UTS), $\sigma_{\text{UTS}}$, increases with increasing the rolling reduction, but the ductility decreases. $\sigma_{\text{UTS}}$ increases from 288 MPa to 351, 477, 607, 690, 734, and 736 MPa, increasing the rolling reduction. Note that the values for 90%– and 95%-specimens are almost the same. The increase in strength is attributed to the grain refinements and work hardening based on the microstructure observations and XRD measurements. Especially, the changes in mechanical properties of the specimens cold-rolled to over 80% would be strongly associated with the formation of the heterogeneous-nano structure. It was reported that the increase in the volume fraction of the eye-shaped regions increased UTS.13,14 However, the strength of the 95-specimen almost remained-unchanged from the 90%-one, even though the volume fraction of eye-shaped size which cannot be detected using BEIs and EBSD measurements as shown in Figs. 3–5.
3.3 Change in electrical resistivity

Figure 8 shows the rolling reduction dependence of (a) electrical resistivity at 293 K and 77 K, and (b) electrical conductivity (% IACS).

![Figure 8](image)

The drastic increase in the electrical resistivity measured at 293 K monotonically increases around 11.6 Ωm from around 61.6 Ωm at 0% reduction till around 73.2 Ωm at 80% (Fig. 8(a)). When the rolling reduction exceeds 80%, the electrical resistivity drastically increases around 13.7 Ωm and attains around 80.6 Ωm at 95%. At 77 K, the value monotonically increases around 11.5 Ωm from around 39.6 Ωm till around 51.1 Ωm. Then, the value drastically increases around 10.8 Ωm to be around 61.9 Ωm at 95%.

The electrical resistivity measured at 293 K is always around 23 Ωm higher than that measured at 77 K. Since the lattice vibration of metals is suppressed at the liquid nitrogen temperature of 77 K, the suppression of the lattice scattering occurs. The changes in electrical resistivity upon the cold-rolling have almost no temperature dependence since the tendency of electrical resistivity measured at 293 K and 77 K are practically the same. The electrical resistivity should increase with increasing the density of lattice defect caused by the rolling, resulting in the reduction of the mean free path of electrons. The drastic increase in the electrical resistivity on the cold rolling of more than 80% is associated with the development of heterogeneous-nano structure (Figs. 3–5). The shear bands surrounding the rhombus regions consist of ultrafine grains with considerable internal strain, preventing detecting the clear Kikuchi line images. Therefore, electrons should be scattered by the presence of high densities of GBs and dislocations as well as the high internal strain. The change in electrical conductivity at 293 K reduces around 8.1% IACS from around 28.0% IACS down to around 19.9% IACS (Fig. 8(b)). The change in electrical properties was also strongly correlated with the formation of the heterogeneous-nano structure.

4. Conclusions

Cu–30 mass%Zn alloys were subjected to cold rolling up to 95% reduction in thickness. Microstructural observations, and the investigations of the mechanical and the electrical properties were performed. The obtained main results were summarized as follows.

(1) The heterogeneous-nano structure with the “eye-shaped” microstructure formed when the rolling reduction exceeded 80%. The volume fraction of the heterogeneous-nano structure became largest at 90% reduction.

(2) Ultimate tensile strength reaches around 735 MPa at 90% and 95% reduction.

(3) The electrical resistivity measured at 77 K increases from around 39.6 Ωm to around 61.9 Ωm. The electrical conductivity at 293 K decreases from around 28.0% IACS down to around 19.9% IACS. The change in electrical properties was accelerated when the rolling reduction exceeded 80%.

(4) The change in mechanical and electrical properties was strongly correlated with the formation of the heterogeneous-nano structure.

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REFERENCES