Development and Microstructure of Cu–Zr Alloy Wire with Ultimate Tensile Strength of 2.2 GPa*

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Round, bar-shaped ingots of hypoeutectic Cu–4 and Cu–5 at%Zr alloys were cast using the copper-mold casting method. The ingots were drawn into wires with a drawing ratio (η) of 5.9 or more. The relationship between the mechanical and electrical properties of these wires as well as their microstructure was investigated. It was found that the Cu–5 at%Zr alloy wire drawn down to 40 µm in diameter with η = 8.6 exhibited an ultimate tensile strength (UTS) of 2234 MPa, 0.2% proof stress of 1873 MPa, total strain to fracture of 4.2%, Young’s modulus of 126 GPa, and electrical conductivity of 16% IACS. As for the Cu–4 at%Zr alloy, it could be wire-drawn down to 27 µm in diameter with η = 9.4.

Both UTS and Young’s modulus increase linearly with η. A nanosized lamellar structure was noticed in the α-Cu and Cu9Zr2 intermetallic compound phases. Furthermore, it was observed that a nanosized amorphous phase was formed within the layers of the Cu9Zr2 intermetallic compound phase. The increase in the strength of the wire-drawn Cu–4 and Cu–5 at%Zr alloy is due to the synergistic effects resulting from the development of deformation twins in the α-Cu phase and the formation of the nanosized lamellar structure in the α-Cu and Cu9Zr2 intermetallic compound phases.

High electrical conductivity of 16% IACS was obtained for the wire-drawn Cu–5 at%Zr alloy. This high value can be attributed to the low density of dislocations in the α-Cu phase. [doi:10.2320/matertrans.M2012064]

Keywords: copper–zirconium alloy; hypoeutectic alloy; wire-drawing; high strength; high electrical conductivity; microstructure

1. Introduction

Recently electronic devices have undergone extreme miniaturization with the simultaneous addition of even greater levels of functionality. Further development along this path requires Cu alloys that have both high strength and high electrical conductivity. In the case of Cu alloy wires, which are the focus of the present study, most efforts were focused on producing materials with high electrical conductivity.1–3,5 Few studies have aimed to develop high strength wires. Higher strength is desirable in thin Cu alloy wires to prevent them from breaking during post-drawing processes such as twisting as this eventually leads to a reduction in productivity.

Several studies describing the production of new copper-based composite materials and the characteristics of these materials have been reported. These materials include cold-drawn wires of Cu–Ag alloys with an eutectic lamellar structures, Cu–Cr, Cu–Fe and Cu–Nb alloys with a small amount of hard metal particles dispersed in their matrices; yellow brass or Cu with solid-phase-sintered tungsten, and Cu with Al2O3 dispersed by an internal oxidation method.1–3

Sakai et al. studied Cu–Ag alloys prepared by adding Ag to Cu.12–15 This resulted in the formation of fine primary Cu and fine eutectic Cu and Ag phases during the casting. In order to increase the strength of the alloys, these primary and eutectic phases were then elongated into fiber structures by cold wire-drawing or rolling. They were then able to achieve alloys with both high electrical conductivity and high strength by the precipitation of Ag and Cu dissolved in both phases through multistage thermal treatments in a vacuum or inert gas atmosphere during the cold-working process.15 On the other hand, Bevk et al.9 reported a high strength Cu–12.5 at%Nb alloy that was heavily worked — the reduction was 99.999% — to form 18.2 vol% of Nb filaments in the matrix. The alloy had an ultimate tensile strength (UTS) of 2230 MPa and a 0.2% proof strength of 1750 MPa at room temperature. However, their study did not describe electrical conductivity of this alloy.

The authors of the present study have previously investigated the microstructures as well as the electrical and mechanical properties of rapidly solidified and wire-drawn materials of hypoeutectic Cu–Zr alloys.16–18 They have also reported the following facts: the UTS and 0.2% proof strength increase with the drawing ratio; a Cu–5 at%Zr alloy wire with a drawing ratio (η) of 5.9 has an UTS of 1773 MPa and electrical conductivity (EC) of 24% IACS; and α-Cu and Cu9Zr2 intermetallic compound phases form lamellar structures with their layers in the eutectic phase, which have a width of about 20 nm.19

In this study, ingots of hypoeutectic Cu–4 and Cu–5 at%Zr alloys were drawn into wires with a drawing ratio of 5.9 or more. The electrical and mechanical properties of these wires were examined and the relationship between these properties and the microstructure of the wires was investigated.

2. Experimental Procedures

2.1 Preparation of specimens

Cu (99.99 mass%) and Zr (>99.95 mass%) were melted using the arc-melting method and cast in a copper mold shaped like a round bar. The resulting Cu–4 and Cu–5 at%Zr alloy ingots were drawn into wires, with starting dimensions of 3 mm in diameter and 60 mm in width, were solidified rapidly. A Cu–4 and Cu–5 at%Zr alloy ingot, weighing 20 g,
were crushed and part of the crushed ingot was put into a quartz nozzle that had an inner diameter of 12 mm and a pouring hole with a diameter of 1.2 mm. The alloy was melted using a high-frequency induction heating furnace in an Ar gas atmosphere and cast into a copper mold with a rod-shaped cavity by applying a pressure of 0.5 MPa. These cast bars were cold drawn into wires 0.5 mm in diameter by using cemented carbide dies; thereafter, diamond dies were used for continuous cold wire-drawing. The drawing ratio \( \eta \) during the process was calculated using eq. (1), where \( A_0 \) and \( A \) are the original and final cross-sectional areas of the drawn wire specimens, respectively.

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\eta = \ln\left(\frac{A_0}{A}\right) \tag{1}
\]

### 2.2 Tensile test, conductivity measurement, and structural observations

The tensile test of the Cu–Zr drawn wires was conducted at room temperature using a multifunctional tensile testing machine conforming to JIS B7721 Class 0.5 (Shimadzu AG-I) with a gage length of 100 mm and cross-head speed of 1 mm/min (corresponding to a strain rate of \( 1.7 \times 10^{-4} \text{s}^{-1} \)). Young’s modulus was measured by using a resonant-method-based device with a cantilever mechanism (Nippon Techno-Plus TE-Series). The electrical conductivity (EC) was calculated by eq. (2), where \( 1.7241 \mu\Omega\text{cm} \) is the electrical conductivity of a sample conforming to the International Annealed Copper Standard (IACS) at 293 K and \( \rho \) is the electrical resistivity of the specimen measured by a four-probe technique at room temperature.

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EC (\%\text{IACS}) = \frac{1.7241}{\rho} \times 100 \text{ (\%)} \tag{2}
\]

Prior to being observed with a scanning transmission electron microscope (STEM), the wire-drawn specimens were first processed to a thin-film form by a focused ion-beam thinning apparatus (Hitachi FB2000A) at an acceleration voltage of 30 kV and then ion-milled using a precision ion polishing system (Gatan PIPS Model-691). The STEM observations were made using a field emission transmission electron microscope (FE-TEM) (JEOL JEM-2010F) equipped with a scanning electron beam imaging device working at an acceleration voltage of 200 kV and a nanoelectron beam of size about 1 nm. In addition, energy-dispersive X-ray spectroscopy (EDX) analysis was also performed using an X-ray microanalysis system (NORAN VANTAGE).

### 3. Results

Round, bar-shaped ingots of Cu–4at%Zr and Cu–5at%Zr alloys, 3 mm in diameter and 60 mm in length, were drawn into wires. It was possible to draw down the Cu–4at%Zr alloy bars to a diameter of 27 \( \mu \)m at \( \eta = 9.4 \) (equivalent to a cross-section reduction rate of approximately 99.992\%). and the Cu–5at%Zr alloy bars to a diameter of 40 \( \mu \)m at \( \eta = 8.6 \) (equivalent to a cross-section reduction rate of 99.990\%). These facts suggest that it becomes more difficult to wiredraw the Cu–Zr alloy as its Zr content increases.

Figure 1(a) shows the scanning electron microscopy (SEM) micrographs of the surface of the Cu–5at%Zr alloy wire drawn with \( \eta = 8.6 \) and its transverse cross-section is shown in Fig. 1(b). The surface appears to be smooth except for a few scratches caused by friction against the cemented carbide die. One can notice the perfectly circular shape of the cross-section. These results suggest that the Cu–5at%Zr alloy has sufficient drawability.

Figure 2 shows the nominal stress–strain curve for the drawn 40-\( \mu \)m-thick Cu–5at%Zr alloy wire with \( \eta = 8.6 \). The small offset in the nominal strain was caused by the slackening of the wire specimen when it was set in the tensile testing machine. The 0.2% proof stress was measured at the point of 0.2% offset from the nominal strain. Table 1 shows the ultimate tensile strength, 0.2% proof stress, and total strain to fracture, all measured from Fig. 2; Young’s modulus measured by resonant-method-based device with a cantilever mechanism; and the electrical conductivity. For comparison, experimental results by Bevk et al. are also given in the Table 1. Their results show the characteristics of a Cu–12.5at%Nb alloy wire with a diameter of 24 \( \mu \)m and \( \eta = 11.5 \). This alloy wire had been reported to have the highest UTS to date. However, its electrical conductivity had not been mentioned. The UTS of the Cu–5at%Zr alloy wire is almost the same as that of the Cu–12.5at%Nb alloy wire, whereas the 0.2% proof stress, total strain to fracture, and Young’s modulus of the Cu–5at%Zr alloy wire are 123 MPa higher, about 70% higher, and about 11% lower, respectively.
which is higher than those of commercial Cu–Ti alloys.20,21) This is in conjunction with its ultimate tensile strength (2.2 GPa). It was evident from the results that it was possible to wiredraw the alloy down to a diameter of 27 µm with a strain to fracture (εf) of 4.2%, total strain to fracture (εt) of 8.6 and the Cu–Sn–P alloy wire with an IACS of 1750, 2.45% IACS. This suggests that the UTS of the Cu–Sn–P alloy wire drawn to 8.6% is higher than those of the Cu–4 at%Zr alloy wire drawn to 9.4%. Similar relationships obtained for Cu–3%, Cu–4%, and Cu–5 at%Zr alloy wires by Muramatsu et al. as well as those for typical conventional copper alloys20,21) are also plotted in Fig. 4. The electrical conductivity of the Cu–5 at%Zr alloy wire in the present study with η = 8.6 is higher than those of the Cu–Sn–P and Cu–Ti alloys and almost the same as that of the Cu–Be–Co (C17200) alloy, which is considered a high strength material. However, UTS of the alloy wire is three times larger than that of the Cu–Sn–P alloy wire. The Cu–5 at%Zr alloy wire was tested for large values of η. It was evident from the results that it was possible to wiredraw the alloy down to a diameter of 27 µm with η = 9.4 (equivalent to a cross-section reduction rate of approximately 99.992%). The UTS, Young’s modulus, and electrical conductivity of this 27-µm-thick wire were 1774 MPa, 122 GPa, and 20% IACS, respectively. Figure 3 shows the UTS and Young’s modulus as functions of the drawing ratio η. Figure 3 also shows the UTS results by Muramatsu et al. The UTS (σUTS) and Young’s modulus (E) are proportional to the drawing ratio (η). This suggests that the UTS of the Cu–5 at%Zr alloy wire could be increased beyond 2.2 GPa if further wiredrawing were possible. However, it is understood that the drawing ratio of Cu–5 at%Zr alloy is limited to around 8.6.

Furthermore, the drawability of the Cu–4 at%Zr alloy was tested for large values of η. It was evident from the results that it was possible to wiredraw the alloy down to a diameter of 27 µm with η = 9.4 (equivalent to a cross-section reduction rate of approximately 99.992%). The UTS, Young’s modulus, and electrical conductivity of this 27-µm-thick wire were 1774 MPa, 122 GPa, and 20% IACS, respectively. Figure 3 shows the UTS and Young’s modulus as functions of the drawing ratio η. Figure 3 also shows the UTS results by Muramatsu et al. The UTS (σUTS) and Young’s modulus (E) are proportional to the drawing ratio (η). This suggests that the UTS of the Cu–5 at%Zr alloy wire could be increased beyond 2.2 GPa if further wiredrawing were possible. However, it is understood that the drawing ratio of Cu–5 at%Zr alloy is limited to around 8.6.

Figure 4 shows the relationship between UTS and electrical conductivity for the Cu–5 at%Zr alloy wire with η = 8.6 and the Cu–4 at%Zr alloy wire with η = 9.4. Similar relationships obtained for Cu–3%, Cu–4%, and Cu–5 at%Zr alloy wires by Muramatsu et al. as well as those for typical conventional copper alloys20,21) are also plotted in Fig. 4. The electrical conductivity of the Cu–5 at%Zr alloy wire in the present study with η = 8.6 is higher than those of the Cu–Sn–P and Cu–Ti alloys and almost the same as that of the Cu–Be–Co (C17200) alloy, which is considered a high strength material. However, UTS of the alloy wire is three times larger than that of the Cu–Sn–P alloy wire. The Cu–5 at%Zr alloy wire was tested for large values of η. It was evident from the results that it was possible to wiredraw the alloy down to a diameter of 27 µm with η = 9.4 (equivalent to a cross-section reduction rate of approximately 99.992%). The UTS, Young’s modulus, and electrical conductivity of this 27-µm-thick wire were 1774 MPa, 122 GPa, and 20% IACS, respectively. Figure 3 shows the UTS and Young’s modulus as functions of the drawing ratio η. Figure 3 also shows the UTS results by Muramatsu et al. The UTS (σUTS) and Young’s modulus (E) are proportional to the drawing ratio (η). This suggests that the UTS of the Cu–5 at%Zr alloy wire could be increased beyond 2.2 GPa if further wiredrawing were possible. However, it is understood that the drawing ratio of Cu–5 at%Zr alloy is limited to around 8.6.

4. Discussion

We investigated the microstructure of the Cu–5 at%Zr alloy wire drawn to η = 8.6 to understand the reasons for its high UTS (2.2 GPa) and EC (16% IACS) values.
Figure 5 shows the STEM images of the longitudinal cross-section of the Cu–5 at%Zr alloy wire drawn to $\eta = 8.6$. Figures 5(a) and 5(b) are the bright field (BF) image and the high-angle annular dark-field (HAADF) image, respectively. The BF image indicates that the drawn Cu–5 at%Zr alloy wire has a fine, minute, and elongated lamellar microstructure. It was shown by Muramatsu et al.\textsuperscript{19} that the bright and dark portions of the microstructure are the $\alpha$-Cu phase and the eutectic $\alpha$-Cu and Cu$_2$Zr$_2$ intermetallic compound phases, respectively. The average layer width of $\alpha$-Cu phase was measured by the line intersection technique and found to be 15.0 nm. Deformation twins, indicated by an arrow in Fig. 5, were observed at an angle of 20 degrees to the lamellar direction. The lamellar structure of the $\alpha$-Cu phase, which is 15.0 nm in width, is further subdivided by such deformation twins. These deformation twins were frequently observed in other images as well. It is known that the deformation twins formed in copper alloys contribute to their reinforcement.\textsuperscript{22,23} On this basis, it is assumed that the deformation twins formed in the drawn Cu–5 at%Zr alloy wire also lead to its reinforcement. The HAADF image (b) reveals the bright $\alpha$-Cu phase and the dark Cu$_2$Zr$_2$ intermetallic compound phase. The average layer width of the Cu$_2$Zr$_2$ intermetallic compound phase was 13.0 nm, which was measured by the same technique as used for the $\alpha$-Cu phase. Figure 5 shows that both the $\alpha$-Cu phase and the eutectic ($\alpha$-Cu and Cu$_2$Zr$_2$ intermetallic compound) phase are alternatively piled up with each layer less that less than 15.0 nm in thickness. This indicates a fine and highly dense lamellar structure forms during wire-drawing process. The mixture law based on the lamellar and fibrous structure with nanometer scale is thought to act as a reinforcement mechanism in this alloy system.

Figure 6(a) shows the EDX spectrum recorded from the spot marked with an X or the dark region in Fig. 5(b). The EDX spectrum from the bright region, i.e., the spot marked with a Y in Fig. 5(b) is shown in Fig. 6(b). The observed dark layers are inferred to belong to the Cu$_2$Zr$_2$ intermetallic compound phase because Zr was detected at the point marked with an X. Furthermore, oxygen was simultaneously detected as 29.0 at% O in the Cu$_2$Zr$_2$ intermetallic compound phase because Zr was detected at the point marked with an X. Furthermore, oxygen was simultaneously detected as 29.0 at% O in the Cu$_2$Zr$_2$ intermetallic compound phase. Oxygen has been also detected in the drawn Cu–4 at%Zr alloy wire.\textsuperscript{19} The effect of the oxygen in the Cu$_2$Zr$_2$ intermetallic compound phase on the reinforcement mechanism is still under investigation and will be considered in detail in a future study. On the other hand, in addition to copper, a small amount of oxygen was detected at point Y. The observed bright lamellar structure on the nanometer scale is confirmed as the $\alpha$-Cu phase. Zirconium was not detected.
at this point as its content was lower than the detection limit of STEM/EDX analyses techniques. However, Muramatsu et al.\textsuperscript{19) reported that 0.3 at\% Zr exists in the $\alpha$-Cu phase. Here, the overall atomic number of the Cu$_9$Zr$_2$ intermetallic compound phase became less than 29 because 29.0 at\% O is included in the phase at point X. As a result, the tone of the HAADF image of the $\alpha$-Cu and Cu$_9$Zr$_2$ intermetallic compound phase is reversed.

Figure 7 shows high magnification images of the parts labeled A and B and enclosed within the square in the (a) STEM-BF and (b) HAADF images, respectively in Fig. 5. The bright $\alpha$-Cu phase and dark Cu$_9$Zr$_2$ intermetallic compound phase appear as straight and lamellar on the nanometer scale. The lamellar $\alpha$-Cu phase has weak contrast in itself, but the dislocation substructure with high pile-up density is barely observable in each layer. This fact suggests that most of the propagated dislocations in each layer boundary, are absorbed and the deformation twin consequently disappears.

Figure 8 (a) shows a highly magnified BF image (observed at a magnification of 3,000,000 times) of the portion labeled C in Fig. 7(a) that is enclosed within a square, and Fig. 8 (b) shows the nanobeam electron diffraction (NBD) image of that area recorded with a beam approximately 1 nm in diameter. The lattice image corresponding to a crystal grain was not seen at the zone in the Cu$_9$Zr$_2$ intermetallic compound phase marked with an arrow. The diameter of this zone is approximately 5 nm. The NBD patterns obtained from the zone exhibit microcrystal and amorphous-like phases. These diffraction patterns will be investigated in detail in a future study. It was observed that the NBD patterns consist of diffraction spots that may come from the $\alpha$-Cu phase and the Cu$_9$Zr$_2$ intermetallic compound phase. The Cu$_9$Zr$_2$ intermetallic compound phase has tetragonal symmetry with lattice parameters close to those of the cubic system.\textsuperscript{19,24) As a consequence, it shear-deforms with ease during the wire-drawing process. However, when the degree of working for the $\alpha$-Cu phase and the Cu$_9$Zr$_2$ intermetallic
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As shown in Fig. 3, UTS ($\sigma_{UTS}$) and Young’s modulus ($E$) increase linearly with the drawing ratio $\eta$. In order to investigate the reason for this linear dependency, the average layer widths of the $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases of the Cu–4 at%Zr alloy wire drawn with $\eta = 5.9$ and $\eta = 8.6$ (Fig. 9) were measured from the STEM images. The average layer widths of the $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases are 111 nm and 12.0 nm at $\eta = 5.9$ and 49.0 nm and 9.0 nm at $\eta = 8.6$, respectively. These results show that these widths decrease as the drawing ratio increases. In addition to being caused by the mixture law mechanism, this reinforcement at a high drawing ratio seems to be because of the reduction in size of the lamellar Cu$_{9}$Zr$_{2}$ intermetallic compound phases. Furthermore, the correlation between Young’s modulus and the drawing ratio may be because of the formation of the nanosized amorphous structure and the corresponding decrease in the volume fraction of the Cu$_{9}$Zr$_{2}$ intermetallic compound phase, as shown in Fig. 8.

As mentioned above, it is considered that the increase in UTS to up to 2.2 GPa by wire-drawing is because of the synergistic effects of the following: (1) deformation twins; (2) a mixture law based on the lamellar $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases; and (3) the reduction in size of these lamellar phases. In order to further elucidate the reinforcement mechanism, however, it is necessary to observe these microstructures in detail.

The Cu–5 at%Zr alloy wire drawn with $\eta = 8.6$ exhibited good electrical conductivity with a value 16%IACS. This was in conjunction with its ultimate tensile strength of 2.2 GPa and this phenomenon may be attributed to the low density of the dislocations in the $\alpha$-Cu phase.

REFERENCES


5. Summary

Round, bar-shaped ingots of hypoeutectic Cu–4 and Cu–5 at%Zr alloys were cast into a copper mold. This alloy was drawn into wires with a drawing ratio of 5.9 or more. The electrical and mechanical properties of these wires were examined and the correlation between these properties and microstructures of these wires was investigated. It was found that the Cu–5 at%Zr alloy wire drawn with $\eta = 8.6$, which was 40 µm in diameter, reached an ultimate tensile strength (UTS) of 2234 MPa and electrical conductivity (EC) of 16%IACS. The other results are as follows:

(1) The Cu–4 at%Zr alloy could be drawn down into a wire of diameter 27 µm with $\eta = 9.4$. Its UTS, Young’s modulus, and electrical conductivity were 1774 MPa, 122 GPa, and 20%IACS, respectively.
(2) The average layer widths of the $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases reduce from 111 nm and 12.0 nm at $\eta = 5.9$ to 49.0 nm and 9.0 nm at $\eta = 8.6$, respectively. These results suggest that the reduction of the $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases contributes to the reinforcement based on the drawing ratio.
(3) The Cu–5 at%Zr alloy could be drawn down into a wire of diameter 40 µm with $\eta = 9.4$. Its UTS, 0.2% proof stress, total strain to fracture, Young’s modulus, and electrical conductivity were 2234 MPa, 1873 MPa, 4.2%, 127 GPa, and 16%IACS respectively. The wire had minute lamellar structures within the $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases. The average layer widths were 15.0 nm and 13.0 nm. A nanosized amorphous phase was observed in the lamellar Cu$_{9}$Zr$_{2}$ intermetallic compound phase.
(4) The reinforcement by heavy wire-drawing was attributed to the synergistic effects of deformation twins in the $\alpha$-Cu phase, a mixture law based on the lamellar $\alpha$-Cu and Cu$_{9}$Zr$_{2}$ intermetallic compound phases, and the reduction in size of these lamellar phases.

The Cu–5 at%Zr alloy wire drawn with $\eta = 8.6$ exhibited good electrical conductivity with a value 16%IACS. This was in conjunction with its ultimate tensile strength of 2.2 GPa and this phenomenon may be attributed to the low density of the dislocations in the $\alpha$-Cu phase.
11) http://t-kimura03.cc.yamaguchi-u.ac.jp/classic/kaizen01/h13-5m/5m29c.htm