Characteristics of Hypoeutectic Cu–Zr Alloy Rods Manufactured by Vertically Upwards Continuous Casting*1

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This study applied a vertically upwards continuous casting (VUCC) mass-production method to the pilot-scale production of hypoeutectic Cu–xZr (x = 0.25–5 at%) alloy rods. The microstructures of these VUCC rods were investigated and compared with those of rods produced by copper mold casting (CMC). In addition, the wire-drawing ability of the VUCC rods was examined, and the adaptability of the VUCC method to the mass production of hypoeutectic Cu–Zr alloys was fully investigated. The results show that VUCC provides a higher rate of cooling than CMC, with the resulting dendritic microstructure expected to contribute to its arm-spacing refinement. Furthermore, the VUCC rods exhibit good wire-drawing ability. The ultimate tensile strength, total strain to fracture, and electrical conductivity of Cu–2.5Zr (at%) alloy wires with diameter of 13.8 μm drawn from a VUCC rod are 1882 ± 28 MPa, 2.2 ± 0.2%, and 21% IACS (i.e. 21% of the International Annealed Copper Standard conductivity of annealed copper), respectively. The results suggest that VUCC has good potential to be adapted for mass production of hypoeutectic Cu–Zr alloy rods.

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1. Introduction

Ideally, copper alloys manufactured for use in miniaturized electronic devices should exhibit a combination of high strength and high electrical conductivity. The inevitable trade-off between these two properties can prevent this miniaturization. In fact, several studies describing the production of new copper alloy materials and the characteristics of these materials have been reported. These materials include Cu–Cr1–5, Cu–Fe6, and Cu–Nb7 alloys with a small amount of hard metal particles dispersed in their matrices, for instance, yellow brass or Cu with solid-phase-sintered tungsten8,9. Furthermore, drawn Cu–Ag alloy wires10,11 with a eutectic lamellar structure created by casting have also been studied. Sakai et al. studied Cu–Ag alloys reinforced by fiber-like structures in which the primary and eutectic phases underwent elongation during a cold wire-drawing process12–14. In contrast, other efforts have focused on the production of lean Cu alloy materials with high electrical conductivity15,16. However, no copper alloys have yet been able to overcome the trade-off relationship.

Therefore, the authors of this study investigated hypoeutectic Cu–xZr (x = 0.5–5 at%) alloys produced by copper mold casting (CMC) and reported the following characteristics: (i) the fine dendritic microstructure of the as produced Cu–xZr alloys; (ii) the change in Cu–xZr alloy microstructure after heavy wire-drawing to form a lamellar structure of nanometer-scale layers of copper and a Cu/Cu–Zr intermetallic eutectic phase; inductive to the increase in the wire strength with maintaining its electrical conductivity; and (iii) the fine balance between strength and electrical conductivity exhibited by the drawn wires17–20. As a result, the ultimate tensile strength and the electrical conductivity of these Cu–xZr alloy wires reached the value range from a strength of 600 MPa corresponds to a conductivity of 90% IACS to a strength of 2234 MPa corresponds to 16% IACS, which sufficiently overcome the above-mentioned trade-off. Moreover, the maximum value of the strength is comparable to that of the high tensile strength steel (HTSS) and pre-stressed concrete (PC) steel wires21. These properties are attributed to the development of nanometer-scale fibers for fiber-reinforcement and to a very low dislocation density and the absence of other phase boundaries in the Cu matrix for maintaining the high electrical conductivity. Despite the advantages offered by cast alloys, the 3-mm-inner-diameter mold sizes available for CMC greatly limit the solidification volume, thus making CMC unsuitable for industrial use.

In order to overcome the size limit in this study, we focused on applying the vertically upwards continuous casting (VUCC) method, which is practically applied for the mass production of oxygen free copper, yellow brass, aluminum, and its alloy rods5,22,23. In addition, we focused on the microstructure resulting from the solidification rate, and contributable to good wire-drawing ability and the final wire properties. This is because the VUCC method is useful to prevent the semi-solid phase from making micro-shrinkage with its high cooling rate and to possibly prepare the fine dendritic microstructure with resulting a development of the same nanometer-scale fibrous structure as the CMC during wire-drawing. The microstructure of the 15-mm-diameter hypoeutectic Cu–xZr (x = 0.25–5 at%) alloy rods produced to the pilot-scale manufacturing by the VUCC was investigated and compared with that of the CMC rods. It has become clear that VUCC provided a higher rate of cooling than CMC, with the resulting dendritic microstructure refinement. In addition, the mechanical and electrical properties of the 13.8-μm-diameter wire drawn from the VUCC rod were examined, and these results have made it clear that the VUCC is a good potential mass-production method of hypoeutectic Cu–Zr alloys.

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2. Experimental Procedures

Cu–Zr alloy rods were produced by a pilot-scale VUCC facility at Rautomead Ltd., Dundee, Scotland, UK. The VUCC equipment is illustrated in Fig. 1. Feedstock specimens were first prepared from (a) 8-mm-diameter oxygen-free copper (OFC) wires and (b) 13-mm-diameter Cu–50Zr (mass%) cored-wires purchased from Affival SAS, Solesmes, France. The cored wires were selected because their melting point of 1168 K is much lower than that of 2125 K for pure Zr, which makes it easier to use them as the source of zirconium for incorporation in copper. The preparation of this feedstock was controlled by varying the individual intermittent injection speed of both components (a) and (b) to produce an alloy composition of Cu–xZr (x = 0.25–5 at%), which was melted in a 500-kg-capacity graphite crucible at a constant temperature of 1573 K. Hereafter, Cu–Zr alloys with different compositions are referred to simply as Cu–xZr, with all values of x in at% unless stated otherwise. Oxidation of the molten metal surface was suppressed using a graphite die insert wrapped in a copper tube, continuous casting was performed by pulling vertically upwards. Graphite dies with inner diameters of 8, 10, and 15 mm and thermal conductivity of 149 W m⁻¹ K⁻¹ were prepared, and their inner surface was finished with a surface roughness of ISO grade N6. In this method, an average thermal-gradient of more than 3 K/mm over a length of approximately 300 mm on copper mold was obtained to transition from liquid to solid phases. This is because the breakout ring was not used to prevent the melt from breaking. As a result, a more rapid solidification could be obtained by VUCC than could be obtained by conventional horizontal-continuous-casting (HCC). The cast rod was pulled upwards by servo-controlled pinch rollers using an intermittent cycle (repeated pull-and-stop motion at constant intervals). The average upwards-casting speed was 1375 mm/min, and the ratio between the pull and dwell times was kept within 1:3 to 1:4. More than 200 kg of rod was continuously cast and coiled for each alloy composition.

Each of the VUCC rods was subsequently drawn down to 0.6 mm in diameter through a combination of hot or cold swaging, combination-rolling, and drawing with cassette roller dies. The draw-ability of each material was then investigated by further wire drawing to an arbitrary diameter using a continuous wire-drawing process. The final wire was drawn from a 15-mm-diameter VUCC rod down to 13.8-μm-diameter at a drawing ratio (η) of 11.7. This ratio is defined by the equation \( \eta = \ln (A_0/A) \), where \( A_0 \) is the original cross-sectional area of the rod and \( A \) is the final cross-sectional area of the wire.

Chemical analysis of the VUCC rods was conducted using inductively coupled plasma–atomic emission spectroscopy (ICP–AES). Microstructural examination was carried out using laser microscopy, field-emission scanning electron microscopy (FE-SEM), and field-emission transmission electron microscopy (FE-TEM). Individual phases in each of the cast rods were identified through X-ray diffraction (XRD). The electrical conductivity (EC) of the rod and wire specimens was determined from their electrical resistivity, measured using a mono-probe for the rods and the four-probe technique for the wires. The values of EC were calculated by EC (% IACS) = (0.017241/\( \rho \)) × 100, where 0.017241 μΩ·m is the electrical conductivity of a standard annealed copper sample according to the International Annealed Copper Standard (IACS), and \( \rho \) is the electrical conductivity of the specimens. The hardness was measured using Vickers hardness testing with an applied force of 0.98 N. Tensile tests were performed on the drawn wires at room temperature using a multifunctional tensile-testing machine that conformed to the JIS B7721 Class 0.5 standard (Shimadzu AG-I) and had a gage length of 100 mm and cross-head speed of 1 mm/min (corresponding to a strain rate of 1.7 × 10⁻⁴ s⁻¹). The ultimate tensile strengths and total strains to fracture were examined using several specimens to obtain the accurate tensile properties. The total strain was measured with the cross-head displacement from zero to the fracture strain.

3. Results

3.1 Appearance and surface characteristics of VUCC rods

Figure 2 shows the appearance of the Cu–5Zr alloy rods produced by VUCC. Rods diameter of 8, 10, and 15 mm are shown. Oscillation marks consistent with cold shuts during continuous casting were clearly aligned on the rod surface. Figure 3 shows a laser-microscopic image of the longitudinal cross section of the 15-mm-diameter Cu–0.25Zr alloy rod (in Fig. 2(c)). The arrow indicates the upwards casting direction. One of the small notches generated between the oscillation marks can be seen in Fig. 3. Figure 4 shows the relationship between the notch depth of the longitudinal cross-section, measured by laser microscopy and the Zr content. The hardness of the 12-mm-diameter rods that contained more than 2 at% Zr was in the range of 172–230 MHv, and their notch depth was in the range of 0.1–0.55 mm. In contrast, the hardness and notch depths of 15-mm-diameter rods containing...
less than 1 at% Zr were 81–101 MHv and 0.3–0.8 mm, respectively. These results suggest that the notch depth did not depend on the Zr content when it was less than 1 at%, but the hardness had an inverse correlation with the Zr content when it was above 2 at%. Figure 5 shows XRD profiles obtained from transverse cross sections of the 8-, 10-, and 15-mm-diameter rods of Cu–Zr alloys produced by VUCC. These profiles indicate that all of these rods had a dual-phase structure consisting of a Cu phase and a Cu$_5$Zr intermetallic compound, which is comparable to the structure of Cu–0.5Zr, Cu–1Zr, and Cu–2Zr (at%) alloys produced by CMC.

### 3.2 Chemical and microstructural analysis of VUCC rods

The ICP–AES analysis was conducted to investigate the alloy composition stability of the 7–11 cast-rod specimens. They were cut at intervals of 3 m from each Cu–Zr alloy rod prepared by VUCC, which had a diameter of 15 mm and length of 21–33 m. The analysis results are summarized in Table 1. The difference between the average measured value of Zr content and the target content varied from 2% to 12%, and the standard deviation in measured values of each target Zr concentration ranged from 1% to 7%. It is clearly evident that the alloy composition of the 15-mm-diameter and approximately 30-m-long Cu–Zr alloy rods could be efficiently maintained with a high tolerance during preparation by VUCC from the Cu–50Zr (mass%) mother alloy.

Figure 6(a)–(c) show SEM–backscattered electron imaging (SEM–BEI) micrographs of the longitudinal cross section of the Cu–5Zr alloy rods produced by VUCC with diameters of (a) 8, (b) 10, and (c) 15 mm.

![Cu–5Zr alloy rods produced by VUCC with diameters of (a) 8, (b) 10, and (c) 15 mm.](image)

![Laser-microscopic image of the longitudinal cross section of the 15-mm-diameter Cu–0.25Zr alloy rod produced by VUCC.](image)

![Relationship between notch depth observed on the longitudinal cross section and Zr content of Cu–xZr alloy rods, produced by VUCC, with two different diameters (d).](image)

### Table 1

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<th>x (at%)</th>
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of the VUCC Cu–5Zr alloy rods with diameters of 8, 10, and 15 mm. Each specimen exhibited a typical dendritic microstructure, which consisted of dark (primary $\alpha$-Cu) and bright (eutectic) phases. As shown in Fig. 5, the eutectic phase consisted of $\alpha$-Cu and Cu$_5$Zr intermetallic compound phases. It can be observed in Fig. 6 that the secondary dendritic arm spacing (DAS) increased with an increase in the rod diameter, indicating that the cooling rate during solidification decreased with increasing rod diameter.

Figure 7 shows the relationship between the diameter and secondary DAS of Cu–5Zr alloy rods produced by VUCC. This secondary DAS was calculated from the average of values measured for the quadruplex arms at five points in the images of Fig. 6. For comparison, the data for Cu–4Zr alloy rods produced by CMC$^{24}$ are also shown. It can be seen that a 4-mm-diameter rod produced by CMC had a DAS value of 3 $\mu$m, whereas the same DAS value was obtained for an 11-mm-diameter rod produced by VUCC. This suggests that VUCC rods solidified at a faster rate and, therefore, had a much finer dendritic microstructure.

### 3.3 Wire-drawing ability and characteristics of as-drawn wires

Figure 8(a) shows an SEM micrograph of a 13.8-$\mu$m-diameter Cu–2.5Zr alloy wire; Fig. 8(b) shows a high-magnification image of the section indicated by an arrow in Fig. 8(a). The image shows that the Cu–Zr alloy wire produced from the VUCC rod had a smooth surface without any crack, suggesting that the VUCC rod had good wire-drawing ability. Figure 9 shows the nominal stress-strain curve of this 13.8-$\mu$m-diameter wire, which was measured six times to obtain the accurate tensile properties. Error bars indicate the range of minimum and maximum flow stresses at an each strain. The small offset in the initial stress was caused by the slacking of the warped wire specimen when it was set straight in the tensile testing machine. The ultimate tensile strength ($\sigma_{UTS}$), total strain to fracture ($\varepsilon_f$), and electrical conductivity (EC) of the 13.8-$\mu$m-diameter Cu–2.5Zr alloy wire created from the VUCC rod and a 27-$\mu$m-diameter Cu–4Zr alloy wire produced from a CMC rod$^{19}$ are listed in Table 2. Standard deviation of $\sigma_{UTS}$ and $\varepsilon_f$ are also shown in the table.

The $\sigma_{UTS}$ and EC values of the VUCC Cu–2.5Zr alloy wire
are comparable with those of the CMC Cu–4Zr alloy wire because of its higher drawing ratio, even though its Zr content is lower than the CMC alloy wire. This suggests that the VUCC rod had better wire-drawing ability than the CMC rod, and this led to both high strength and high electrical conductivity.

4. Discussion

In this study, we investigated (1) the cause of the inverse correlation between the notch depth and Zr content of the VUCC rods, (2) the actual cooling rate of the VUCC rods, and (3) the reason the VUCC rods exhibited good wire-drawing ability.

(1) The Cu–Zr binary phase diagram indicates that the maximum temperature gap of the solid–liquid coexistent region for a hypoeutectic Cu–xZr (x = 0.25–5 at%) alloy is approximately 45 K. Therefore, the sump-shape of a cast rod produced by VUCC at a constant pull-up rate and containing less than 1 at% Zr differed from that of the rod containing more than 2 at% Zr. Figure 10 illustrates the different solidification states in the graphite die for alloy rods with low and high Zr content. The liquid, semi-solid, and solid portions of the alloy and the graphite die are identified by A, B, C, and D, respectively. When region B becomes larger in Fig. 10(a), its solidification shell becomes thinner between regions B and D. In contrast, when region B is smaller in Fig. 10(b), the shell becomes thicker. However, as shown in Fig. 4, the Vickers hardness of the solid phase (represented by C in Fig. 10) in the alloy with low Zr content was lower than that of the alloy with high Zr content. As a result, the surface of the low-Zr solidification shell in Fig. 10(a) can be more easily notched than that of the high-Zr solidification shell in Fig. 10(b), which appears to be the reason for the inverse correlation between the notch depth and Zr content.

(2) Fig. 11 shows the relationship, reported by Simizu et al., between the dendritic cell size (DCS) and cooling rate of Cu–11Ni alloy rods produced by CMC. It also shows the relationship between the secondary DAS and cooling rate of Cu–5Zr alloy rods produced by VUCC. The cooling rate of the VUCC rods was calculated using eq. (1) derived from similar relations in CMC rods:

\[ Y = 0.0203X^{-0.534} \]  

Here, \( X \) and \( Y \) are the cooling rate (K·s\(^{-1}\)) and DCS value (\( \mu m \)), respectively, of Cu–11Ni alloy rods produced by CMC.

Spear et al. proposed using the secondary DAS, dendritic cell interval (DCI), or DCS as a crude density index of the dendritic structure. In contrast, Simizu et al. reported that the size of features of the dendritic structure of Cu–11Ni alloy rods produced by CMC followed the order of DCS < DCI < DAS, and they adopted the DCS to derive eq. (1). In our study, the Cu–5Zr alloy rods produced by VUCC exhibited a similar dendritic structure, but the measured DCS and DCI values varied widely because of the large area ratio of their eutectic phases. Therefore, we adopted the DAS value to estimate the cooling rate. The DAS values of 8-, 10-, and 15-mm-diameter Cu–5Zr alloy rods produced by VUCC (shown in Fig. 6) were 2.2, 2.7, and 4.0 \( \mu m \), respectively; thus, the cooling rates of these VUCC rods, as calculated by eq. (1), were 1562, 3261, and 4785 K/s, respectively. The relationship between the DAS and cooling rate is plotted as the dashed line in Fig. 9. This line can be extended to form a straight line with the data reported by Simizu et al. for Cu–11Ni alloy rods, suggesting the appropriateness of eq. (1). Figures 7 and 11 also show that the cooling rate of the VUCC rods was higher than that of the CMC rods, which means that
the microstructure of the VUCC rods was finer than that of the CMC rods. (3) Fig. 12(a) shows an SEM–BEI image of a transverse cross section of the Cu–5Zr alloy rod produced by VUCC; Fig. 12(b), (c), and (d) show Kikuchi patterns obtained at the points indicated by the arrows marked X, Y, and Z, respectively, in Fig. 12(a). The similarity of the channelling patterns of these Kikuchi lines means that the material had the same orientation at points X, Y, and Z. The same microstructure was obtained for the Cu–0.5Zr, Cu–1Zr, and Cu–2Zr alloy rods produced by VUCC. Figure 13 shows a high-magnification bright-field (BF) TEM image of a eutectic phase (which consisted of α-Cu and the intermetallic compound Cu5Zr) had the same local orientations. In addition, both phases of the eutectic phase exhibited fine layered structures. As a result, the α-Cu and cubic Cu5Zr intermetallic compound phases of the eutectic phase were easily deformed simultaneously when the α-Cu phase was deformed during wire-drawing. This seems to be the reason for the good wire-drawing ability exhibited by hypoeutectic Cu–Zr alloy rods produced by VUCC as well as the rods produced by CMC.

5. Summary

The vertically upwards continuous casting (VUCC) mass-production method was applied to the pilot-scale manufacturing of Cu–Zr alloy rods. The microstructure of these VUCC rods was subsequently investigated. In addition, the wire-drawing ability of the VUCC rods was examined, and the ability of the VUCC method to mass-produce hypoeutectic Cu–Zr alloys was fully investigated. The following results were obtained:

(1) VUCC provided a higher rate of cooling than CMC, with the resulting dendritic microstructure expected to contribute to its arm-spacing refinement.

(2) The VUCC rods exhibited good wire-drawing ability.

(3) The ultimate tensile strength, total strain to fracture, and electrical conductivity of the 13.8-μm-diameter Cu–2.5Zr alloy wire created from a VUCC rod were 1882 ± 28 MPa, 2.2 ± 0.2%, and 21% IACS, respectively.

(4) VUCC is a good potential method for the mass production of hypoeutectic Cu–Zr alloy wires.

REFERENCES