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Influence of Phosphorus Content and Preheating Conditions on Grain Size of Cu-DHP Copper Tubes

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Abstract

"Cu-DHP" copper tubes are used in sanitary, plumbing and heat exchanger applications. For drawability and forming processes, grain size is an important factor. Grain size is affected by the process conditions and chemical content. The aim of this study is to examine the effect of phosphorus content on Cu-DHP copper tube products. For this examination, four copper billets with different phosphorus content were used to produce 9.52x0.30 mm copper tubes. The copper billets which are 305 mm in diameter and 580 mm in length were preheated in furnaces and the hot direct extrusion method was used for mother tube production. Shortened preheating time resulted in finer grain size in mother tubes. Mother tubes were cold drawn to the final dimension in subsequent steps and annealed at recrystallization temperature with the same parameters. Grain sizes of annealed 9.52x0.30 mm copper tubes are in the range of 17 to 20 µm. For the final tube dimensions, high amount of cold drawing ratio diminished the effect of the prior grain size of the mother tubes. According to the result of inspections, it is concluded that in cold-drawn and annealed products, phosphorus content has a grain coarsening effect on the final product.

1. Introduction

The oldest metal on the earth is copper which has many superior properties like strength, ductility and hardness. It is also malleable and can be joined easily. High thermal and electrical conductivity makes it indispensable for wiring, tubing, terminals, catenary wires, springs, etc. [1].

Copper tubes are used for air-conditioning, refrigeration, sanitary and plumbing applications, where high thermal conductivity is essential. These copper tubes are generally produced from Cu-DHP, deoxidized high phosphorus copper which contains phosphorus in the range of 150-400 ppm according to the BS EN 1057:2006 standard [2]. As reported by Chapman, Cu-DHP is used to avoid hydrogen embrittlement when the material is heated in a reducing atmosphere as in many sorts of welding and brazing processes, which are applied mainly to copper tubes [3].

Production of copper tubes from the extrusion process starts from the continuous copper billet casting process. The electrolytic copper inlet material is melted and chemical composition adjustment is done in a protective atmosphere of high-efficiency induction furnace in conformance to Cu-DHP norms. Samples are taken from the molten copper periodically to control the process. The molten metal transferred from the induction furnace to the casting furnace is continuously cast by a vertical strand caster in the form of billets with the assistance of an automatic feeding and level controlling unit. To protect from oxidation, the surface of the molten metal is covered with charcoal in the furnaces and with lamp black carbon in the tundish. Copper billets are produced in different diameters and lengths by a flying saw synchronized with the casting system [4, 5]. A schematic visual of the vertical continuous casting process is depicted in Figure 1.

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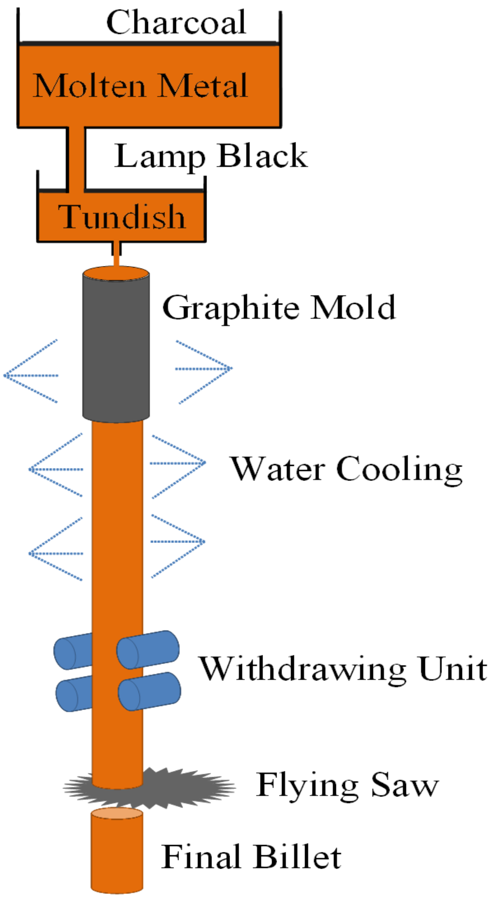


Figure 1. The schematic visual of "Vertical Continuous Casting" process

The next step is pre-heating the billets to around 835˚C before the extrusion process either in induction or gas furnaces. After the pre-heating process, at the extrusion press, a pointed rod called a piercing mandrel is directed towards the center of the billets to form the inside wall of the mother tube (Figure 2) [5].

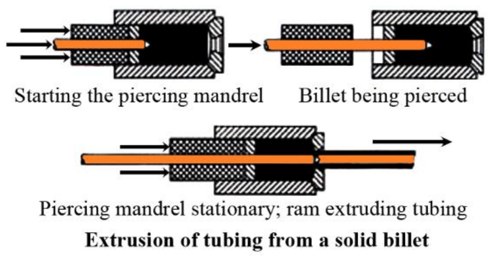


Figure 2. The piercing process of copper billets [5]

The extrusion press consists of a chamber, a die and a hydraulically driven ram. The ram is fitted with a dummy block which has a slightly smaller diameter than the billet. While the ram progresses onward, the copper is constrained over the mandrel and through the hole in the die opening, thus the mother tube is produced [5, 6].

During extrusion, the shell containing copper oxide is extruded through the backside. The shell is later recycled in the refining furnace. While the extruded mother tube comes out from the extrusion press, a conveyor transfers it along on a long run-out table where it is cooled in a solution to prevent oxidation. Additionally, both ends of the mother tube must be sealed to prevent oxidation of inner surface [5, 7, 8].

Tube drawing is the process of pulling tubes to finer sizes through a die made of hardened steel or tungsten carbide. During the drawing process, an inner die which is called as plug that controls the inside diameter precisely is fixed to the copper tube and it works simultaneously with the outer die. The tube is drawn repeatedly for the target tube size. The schematic visual of the drawing step is depicted in Figure 3 [5, 6].

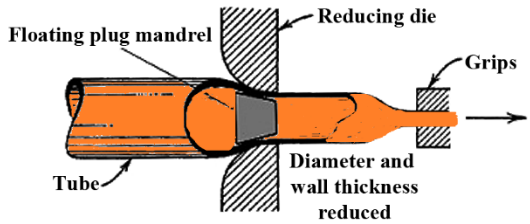


Figure 3. The schematic visual of the tube drawing process with floating mandrel [5]

Tube drawing is a cold-working process that causes the increase of the dislocations and therefore, the hardness. Depending on the usage area, it can be used as hard or in the annealed condition.

As generally known the decreasing grain size which is influenced by the thermal processes the mechanical properties of metals [9]. Grain size is affected by chemical composition, deformation process amount and conditions, and annealing process. For subsequent mechanical processes, grain size is an important factor in preventing unexpected breaking or uneven surfaces in the final product. Grain sizes of the annealed copper tubes become an important factor when the tube will be further mechanically processed. Bending, expanding, flanging and capillary tube drawing processes benefit from smaller grain sizes. Grain refinement is related with the nucleation and growth restriction steps. Alloying elements affect the formation of nucleation sites.

According to the study of Balart et. al. the additions of 150 ppm Ag to 400 ppm P containing DHP-Cu ensured the suitable grain size control. In the study of Cziegler, when Zn, Mg, Fe and Sn have a grain coarsening effect, P has a grain refining effect on copper. P can improve the recrystallization temperature of copper and decrease the grain size [12].

2. Material and Methods

2.1. Extrusion

In this study, Cu-DHP copper billets were produced with a downwards continuous casting method. The copper billets are 305 mm in diameter and 580 mm in length. In casting trials, four copper billets were produced with different phosphorus contents. Their chemical compositions were analyzed with ARL4460 model Optic Emission Spectroscopy and results are given in Table 1.

Table 1. The chemical compositions of the copper billets

Billet No	Cu min. (%)	P (ppm)	Other Elements (ppm)
Cu-DHP BS EN 1057:2006 [2]	99.9	150 - 400	-
A	99.9697	263.7	39.4
B	99.9709	256.2	34.5
C	99.9712	239.1	49.2
D	99.9766	199.8	37.7

The cross sections of the copper billets were etched with 50% nitric acid and %50 water mixture for 2 minutes. The cross sections of etched billets were inspected, and it was observed that the solidification centers of the copper billets are almost centered (Figure 4). Centered solidification is important for the homogeneous flow of the billet in the extrusion process.

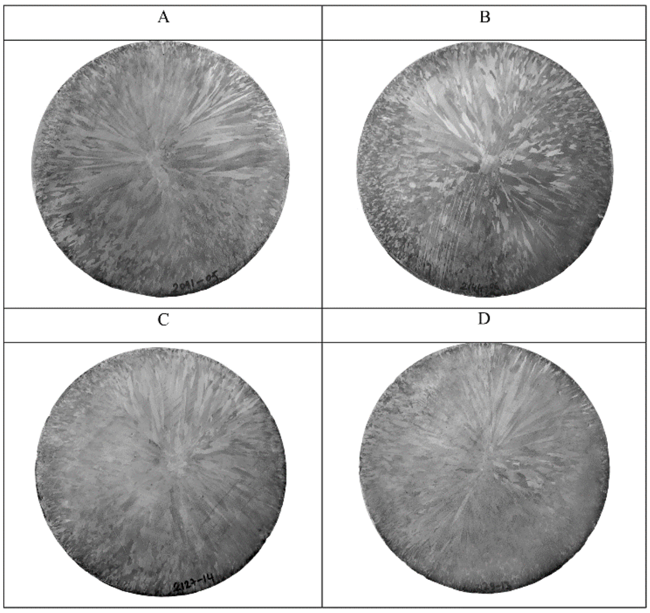


Figure 4. The cross sections of 305 mm diameter copper billets after etching.

For mother tube production with the hot direct extrusion method, the copper billets were heated in gas and induction furnaces consecutively. Afterward the mother tubes were produced from these copper billets in an extrusion press where the process parameters of the heating and extrusion are the same in each production, except the induction furnace heating time ranging between 5 to 13.5 minutes as shown in Table 2.

Samples were taken from the mother tubes with 75 mm outer diameter and 10 mm wall thickness and metallographic specimen preparation was done for the mother tubes that were taken perpendicular to the extrusion direction to determine the grain size. The specimens were inspected with a Jeol JSM 5600 model Scanning Electron Microscope (SEM). Average grain sizes were determined from the cross-section samples of mother tubes according to ASTM E112-13 standard [13], at 120° intervals; from the outer, middle and inner sections of the tube wall to reflect the overall average grain size (Table 2). SEM and average grain size determinations were performed on extruded mother tubes with different phosphorus content. It was observed that the grain sizes were relevant to their induction furnace holding times at the preheating stage before the extrusion. The shortened holding period resulted in a finer grain size and the longer holding periods resulted in coarser grains in mother tubes (Figure 5). The grain sizes are in the range of 60 to 85 μm which is in parallel to holding times in the furnace.

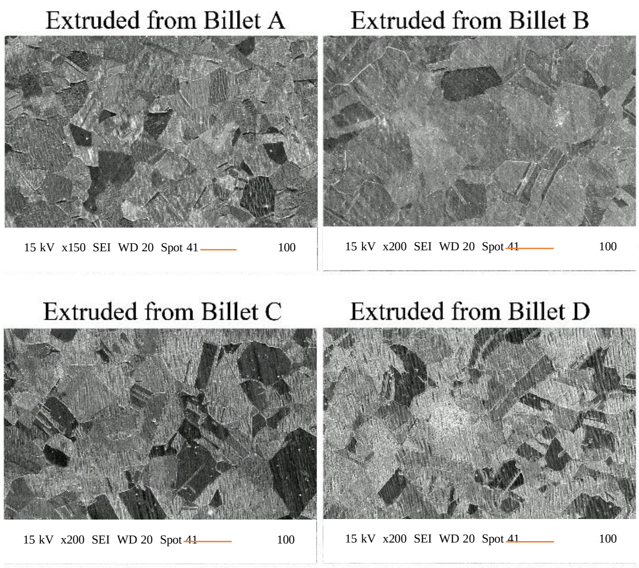


Figure 5. Microstructures of the mother tube cross sections

Table 2. The average grain size of the mother tubes

Mother Tube	Heating Time at Induction Furnace (min)	Grain Size (μm)
Extruded from billet A	13.5	84.62 ± 5.12
Extruded from billet B	5	60.23 ± 2.46
Extruded from billet C	7.5	67.59 ± 5.50
Extruded from billet D	7.5	63.10 ± 4.29

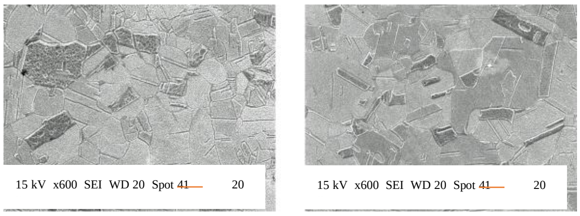
2.2. Cold Drawing and Annealing

From the mother tubes, tubes having 9.52 mm diameter and 0.30 mm wall thickness were produced by cold drawing steps consisting of "break down", "go", "back" and "spinner block drawing" processes respectively, with a total cold reduction of 99.17%. Specimens were taken for hardness and size measurements from the hard-drawn copper tubes. Subsequently, the copper tubes were annealed at recrystallization temperature with same parameters in the Otto Junker tunnel type annealing furnace under protective atmosphere. After the annealing process, the specimens were taken for hardness measurements which were done with Leco model V-100-C1. The results of hardness and size measurements are given in Table 3. The hardness values of the cold drawn and annealed 9.52x0.30 mm Cu-DHP tubes are similar. In the working range of this study, phosphorus content has a slight effect on hardness.

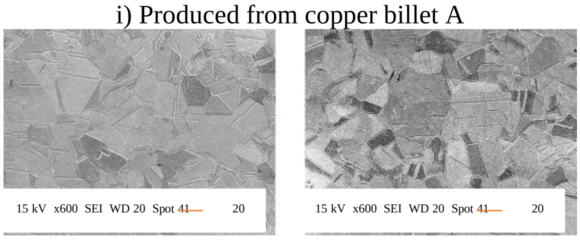
Table 3. Hardness and size measurements of the hard and annealed copper tubes

Copper Billet No	Outer Diameter min. - max. (mm)	Wall Thickness min. -max. (mm)	Average Hardness in Hard Cond. (HV5)	Average Hardness in Annealed Cond. (HV5)
A	9.50 – 9.53	0.29 – 0.33	122.3	36.7
B	9.50 – 9.55	0.28 – 0.33	120.7	36.6
C	9.49 – 9.55	0.28 – 0.33	121.3	35.6
D	9.50 – 9.54	0.29 – 0.33	120.0	34.6

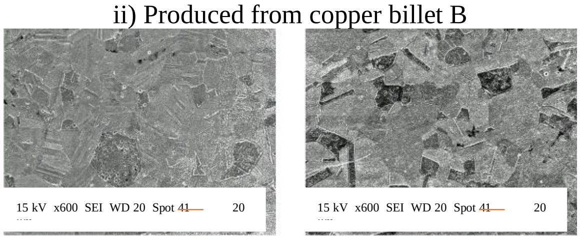
Specimens were taken from the annealed 9.52x0.30 mm final products perpendicular to the tube drawing direction to determine average grain size. The cross sections were metallographically prepared and the microstructure photos were taken with SEM. Microstructure photos of the final copper tubes are shown in Figure 6. Average grain sizes of the annealed 9.52x0.30 mm copper tubes were determined with the same manner as mother tubes and the results are given in Table 4.



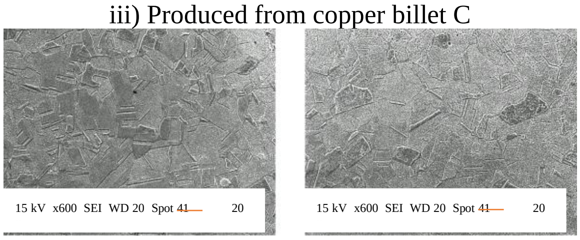
i) Produced from copper billet A



ii) Produced from copper billet B



iii) Produced from copper billet C



iv) Produced from copper billet D

Figure 6. Microstructures of the cold drawn and annealed 9.52x0.30 mm tube cross sections

Table 4. Average grain sizes of the cold drawn – annealed 9.52x0.30 mm copper tubes

Annealed 9.52x0.30 mm Copper Tubes	Grain Size (μm)
Produced from billet A	19.71 ± 0.61
Produced from billet B	19.07 ± 0.93
Produced from billet C	18.45 ± 0.68
Produced from billet D	17.90 ± 0.95

3. Results and Discussion

Grain sizes of annealed 9.52x0.30 mm copper tubes are in the range of 17 to 20 μm. These grain sizes are significantly smaller than their mother tube inlet material, which were between 60 to 85 μm. Heating time in the induction furnace increased in parallel with the grain size of the mother tubes. This shows that the applied high cold drawing ratio of 99.2% diminished the effect of prior grain size of mother tubes. From Figure 5 and Table 2, it can be concluded that the heating time in induction furnace is much more effective despite the amount of phosphorus.

A relation is found between phosphorus content and average grain size in cold drawn and annealed copper tubes that were produced with same process route after the extrusion. In Figure 6 and Table 4, the mother tubes with higher grain sizes had higher grain sizes after cold drawing process. This result shows us the extreme effect of heating conditions on grains size versus phosphorus content. As can be seen in Figure 7, the grain sizes of the final tubes have a polynomially relation with the phosphorus content. The equation that was derived obtained from the graph, can give an idea about the average grain size for a sample which is produced with the same conditions in this study without measuring the grain size experimentally.

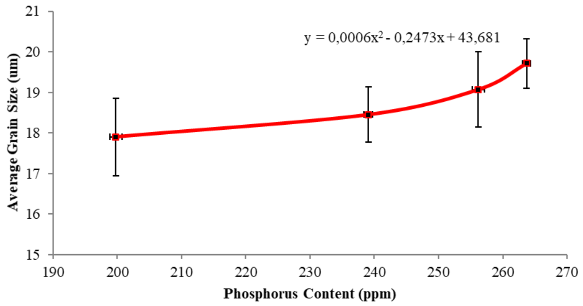


Figure 7. The relation of phosphorus content with average grain size in 9.52x0.30 mm annealed tubes

In Table 3, with the increase of phosphorus content, a slight increase in hardness was detected. This result is in parallel with the study of Zhang et al.

Solid solution strengthening and strain hardening mechanisms promote the dislocation formation. In phosphorus bearing copper alloys, Sandström reported that phosphorus concentration is higher at dislocation centers [14]. When the number of dislocations increases, the movement of the dislocations becomes harder and the internal stored energy increases. The stored energy of cold work aids recovery and recrystallization in annealing [15]. In our study higher dislocation density before the annealing process which was affected by the phosphorus content, has promoted coarsening of the grains. In material with higher phosphorus content, recovery and recrystallization stages are faster thus at the equivalent annealing time and temperature, the remaining time is exerted for grain growth.

4. Conclusions

Cu-DHP tubes with different phosphorus content were produced with same route. The sole difference during the production was the induction furnace holding time before extrusion, which resulted in grain size differences in the extruded mother tube.

After subsequent cold drawing and annealing processes, average grain sizes were compared. The tubes with higher phosphorus content have coarser grains. It was found that influence of prior grain size of the extruded inlet material is negligible, due to the high cold drawing ratio and recrystallization step. It can be interpreted that the differences between the average grain sizes of final copper tubes, which has a high importance for the formability of the final products, are directly related with the phosphorus content. The results about the effect of phosphorus content on grain size is compatible with the study of Cziegler.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors were working for Sarkuysan during this study, but now they are working for different companies.

References

[1] Michel, J., 2013. Introduction To Copper and Copper Alloys, Copper Development Association Inc., https://copper.org/publications/pub_list/pdf/introduction-to-copper-and-copper-alloys.pdf Access Date: December 2, 2022.

[2] BS EN 1057:2006+A1:2010 Copper And Copper Alloys – Seamless, Round Copper Tubes For Water And Gas In Sanitary And Heating Applications.

[3] Chapman, D., 2016. High Conductivity Copper For Electrical Engineering, Copper Development Association – Copper Alliance, **122**, pp.18, 19.

[4] Sarkuysan, 2023. www.sarkuysan.com/en-EN/continuous-billet-casting/152.aspx Access Date: April 24, 2023

[5] Copper, 2023. www.copper.org/publications/newsletters/innovations/1998/09/howdo_tube.html Access Date: April 24, 2023

[6] Dieter, G.E., 1988. Mechanical Metallurgy, SI Metric Edition, McGraw-Hill, pp. 616, 646.

[7] Siegert K., 2004. Extrusion. In Müller, K. (Ed.), Fundamentals Of Extrusion Technology, Giesel Verlag, p. 16.

[8] Laue K., Stenger H., 1981. Extrusion Processes, Machinery, Tooling, American Society For Metals, United States, p. 163.

[9] Clarebrough L. M., Hargreaves M. E., Loretto M. H., 1958. The Influence Of Grain Size On The Stored Energy And Mechanical Properties Of Copper. Acta Metallurgica, **6**, pp 725-735.

[10] Balart M. J., Patel J. B., Gao F., Fan Z., 2015. Grain Refinement Of Dhp Copper By Elemental Additions. International Journal of Cast Metals Research, **28(4)**, pp. 248-256.

[11] Cziegler A., 2015. Aspects of Grain Refinement in Copper Alloys. Master Thesis, University of Leoben.

[12] Zhang Z., Liu H., Hua Y., Zhang B., Hou Z., Li W., Song K., 2024. Study On The Effect Of Phosphorus On Anti-Softening Performance Of, Journal Of Materials Research And Technology, **33**, pp. 2612-2623.

[13] ASTM E112-13 Standard Test Methods for Determining Average Grain Size.

[14] Sandström R., 2014, The Role Of Phosphorus For Mechanical Properties In Copper, https://skb.se/wp-content/uploads/2015/05/1417069-The-role-of-phosphorus-for-mechanical-properties-in-copper.pdf

[15] Hayden H. W., Moffatt W. G., Wulff J., 1965. The Structure And Properties Of Materials Volume III, John Wiley & Sons, p. 169.