

## EFFECTS OF CASTING TEMPERATURE AND MICROALLOYING ELEMENTS ON THE GRAIN STRUCTURE OF DHP COPPER

BALART Maria, PATEL Jayesh, GAO Feng, FAN Zhongyun

*Brunel University, BCAST, Uxbridge, United Kingdom, EU*

[maria.balart@brunel.ac.uk](mailto:maria.balart@brunel.ac.uk), [jayesh.patel@brunel.ac.uk](mailto:jayesh.patel@brunel.ac.uk), [feng.gao@brunel.ac.uk](mailto:feng.gao@brunel.ac.uk), [zhongyun.fan@brunel.ac.uk](mailto:zhongyun.fan@brunel.ac.uk)

### Abstract

The effects of a combined addition of 0.039 % P + 0.015 % Ag as well as a nominal addition of 0.1 % of the de-embrittling elements of copper – B, Mg, Ca, Ti and Zr – to give some variations in contents within the DHP-Cu specification limits on grain size structure at a casting temperature of 1130 °C have been determined and compared to those without the microalloying addition of Ag of 0.015 % obtained at a casting temperature of 1150 °C under TP-1 casting conditions. These results showed that on decreasing the casting temperature from 1150 °C to 1130 °C, the degree of CET increased for DHP-Cu reference with and without microalloying with Ag; the microalloying addition of Ag of 0.015 % to DHP-Cu was essential for grain size control; and that, in comparison to the corresponding DHP-Cu reference cast at 1150 °C and 1130 °C, no further grain refining action was observed due to B, Mg, Ca, Ti and Zr microalloying additions for the conditions studied.

**Keywords:** DHP copper, oxygen free copper, columnar to equiaxed transition, grain refinement, grain growth restriction, de-embrittlement

### 1. INTRODUCTION

Phosphorus-deoxidised, high-residual phosphorus (DHP) Cu contains P in the range 0.015-0.04 wt.% and has a minimum commercial purity of 99.9 % inclusive max. 0.015 wt.% of silver (all percentage compositions here are given in wt.% and ppm in wt. ppm). It has been demonstrated that in DHP-Cu there are many variants on processing route schedules to produce successfully a grain refined microstructure with improved properties [1-3]. For friction stir processing of DHP-Cu plate, for example, it was found that the heat exchange conditions determined the grain size, in that grain size decreased and hardness increased with increasing traverse speed, in bulk processing, and with decreasing rotational speed, in surface processing [1]. For the second example of continuous cast DHP-Cu tube, it was reported that an increased in the casting speed from 1040 mm/min to 1360 mm/min led to a finer grain structure with subsequent improvement of the elongation values from 29 % expanding to 36 % expanding as measured by tube drift expanding test [2].

Our previous work on grain refinement of DHP-Cu by particle inoculation [4] and elemental additions [5] have shown that it was difficult to introduce *in-situ* generated Zr, Ti, Nb, La, Ce, Gd, Nd and W oxide particles and NbB<sub>2</sub> particle additions into the Cu melt as well as grain refinement by combined additions of Ti+B, Zr+B, Al+B and Ca+B [4], and that, among additions of P, Ag, B, Mg, Ca, Ti and Zr within and outside of the DHP-Cu specification limits at a casting temperature of 1150 °C, a nominal addition of 0.1 wt.% Ag gave the strongest grain refining action [5]. It was therefore suggested making the maximum additions of P of 0.04 % and of Ag of 0.015 wt.% to DHP-Cu for adequate grain size control.

Note that, C, P, B, Li and Mg are industrially effective deoxidisers of copper alloy melts, the reaction products being CO / CO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> / 2Cu<sub>2</sub>O.P<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O and MgO, respectively [6]. Thermodynamically, Ca, Ti and Zr can also deoxidise the copper melt. Here, we report the effects of the combined addition of 0.039 wt.% P + 0.015 wt.% Ag as well as the nominal addition of 0.1 % of the de-embrittling elements of copper - B, Mg, Ca, Ti and Zr - [7] to give some variations in contents within the DHP-Cu specification limits on grain size structure at a casting temperature of 1130 °C under TP-1 casting conditions. Those results have been compared and

contrasted with those without the microalloying addition of Ag of 0.015 % obtained at a casting temperature of 1150 °C [5] under TP-1 casting conditions and overall with the corresponding DHP-Cu reference cast at 1150 °C [4] and 1130 °C.

## 2. EXPERIMENTAL

Cu cathode grade A (Cu-CATH-1) was used in this study. High grade Cu-CATH-1 is electrolytically refined to a purity of 99.95 %, containing 0.04 % maximum oxygen. It has a maximum impurity content of 65 ppm and a maximum Ag content of 25 ppm, to conform to BS EN 1978:1998. It is also of interest to note the very low solubility of C in liquid Cu near the melting point of pure Cu [8]. According to the peritectic type Cu-C equilibrium phase diagram that was proposed in Ref. 8, the value of the solubility of C in Cu is 10 at. ppm (1.9 wt ppm) at 1100 °C.

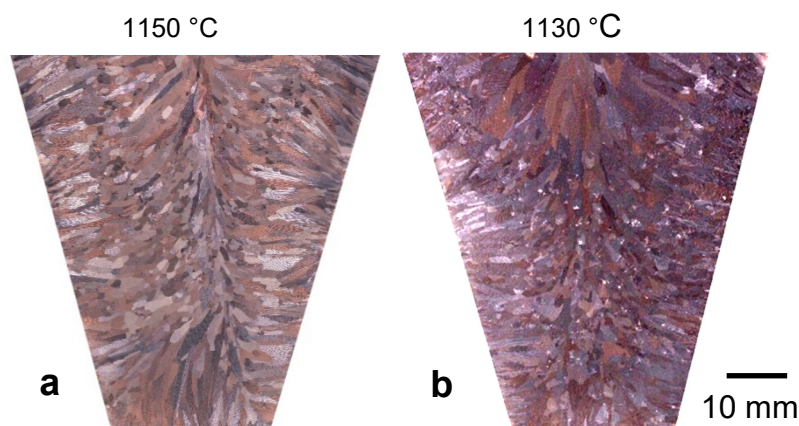
One kilogram of Cu-CATH-1 was remelted for each experiment at ~1200 °C in an A2 size clay-graphite crucible in an induction furnace in air using graphite flake protection on the surface of the melt for deoxidation during melting. Commercially available Cu master alloys and high purity Ag additions as given in **Table 1**, were wrapped in Cu foil and were inserted into the melt at 1200 °C using a graphite plunger just before casting. The melt was always stirred using a graphite rod during the additions and before casting by pouring at 1150 °C or 1130 °C into a standard TP-1 mould [9] preheated to 250 °C, followed by rapidly transferring into the water tank stand where a constant cooling rate of 3.5 K / s was maintained at the centre of a cross-section located 38 mm from the base of the TP-1 sample. Details of all the experiments are also given in Table 1.

The TP-1 casting from each experiment was sectioned longitudinally parallel to its axis. In order to reveal the grain structure, samples were ground and macro-etched using a 1:1 vol. solution of HNO<sub>3</sub> and H<sub>2</sub>O. Samples (1 cm<sup>3</sup>) were located in the mid-section 28-38 mm from the base of selected TP-1 samples and were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES).

## 3. RESULTS AND DISCUSSION

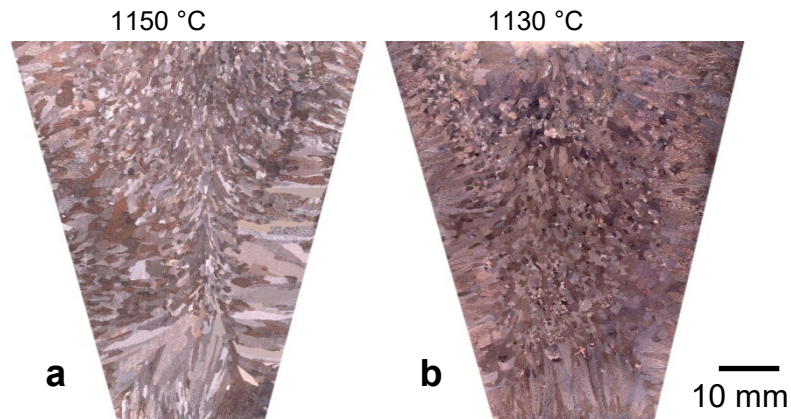
### 3.1. Grain structure of DHP-Cu reference with and without microalloying with Ag

Macrographs of deoxidised DHP-Cu samples with and without a nominal addition of Ag of 0.015 % and cast at 1150 °C and 1130 °C, are shown in **Figs. 1** and **2**. It can be seen that they exhibited some degree of columnar to equiaxed transition (CET) to different extents.



**Fig. 1** Grain structure of DHP-Cu reference without microalloying with Ag: a) cast 1 (0.030 wt.% P, 1150 °C) [4]; b) cast 2 (1130 °C)

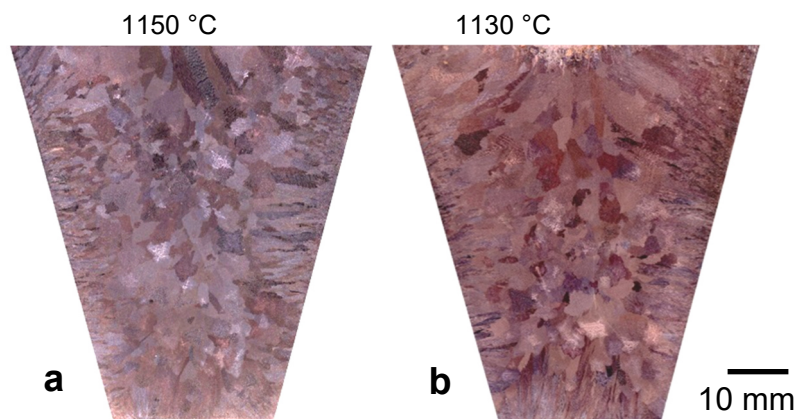
Cast 4 of 0.039 wt.% P + 0.015 wt.% Ag showed the greatest degree of CET – see **Fig. 2 b**). By comparison, a greater degree of CET was obtained: (i) on decreasing the casting temperature from 1150 °C to 1130 °C for a given DHP-Cu reference composition [**Fig. 1 a**] cf. **b**) and **Fig. 2 a**) cf. **b**)] and (ii) with the nominal addition of Ag of 0.015 % at the casting temperatures of 1150 °C and 1130 °C [**Fig. 1 a**] cf. **Fig. 2 a**) and **Fig. 1 b**) cf. **Fig. 2 b**)]. The latter indicated that the microalloy addition of Ag of 0.015 % to DHP-Cu was essential for grain size control. Those results are summarized in **Table 1**.



**Fig. 2** Grain structure of DHP-Cu reference with a nominal addition of Ag of 0.015 %: a) cast 3 (0.039 wt.% P, 0.0143 wt.% Ag, 1150 °C) [4] and b) cast 4 (1130 °C)

### 3.2. Grain structure of DHP-Cu containing P, Ag, B, Mg, Ca, Ti and Zr microalloying additions

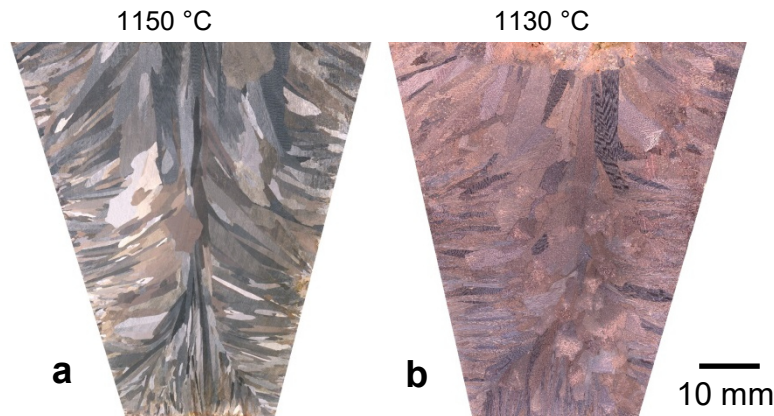
The effects of the de-embrittling elements of copper – B, Mg, Ca, Ti and Zr – [7] in concentrations of 0.085-0.5 wt.% on the grain structure of DHP-Cu without an addition of Ag and cast at 1150 °C have been reported elsewhere as part of another study [5] and some of these results will be presented in this paper for comparison purposes at the two casting temperatures. For given microalloying additions of B, Mg, Ca, Ti and Zr to DHP-Cu, the combined influence of decreasing the casting temperature from 1150 °C to 1130 °C and the nominal addition of Ag of 0.015 % on the grain structure of DHP-Cu are shown in **Figs. 3 to 7**. At both 1150 °C and 1130 °C, for cast 5 of B and cast 6 of B+Ag, the grain structure showed some degree of CET with extremely coarse equiaxed grain sizes (**Fig. 3**), whereas for cast 11 of Ti and cast 12 of Ti+Ag, the grain structure exhibited some degree of CET to a lesser extent compared with those of the corresponding DHP-Cu reference casts 1 and 4 [**Fig. 6 a**] cf. **Fig. 1 a**) and **Fig. 6 b**] cf. **Fig. 2 b**)], respectively.



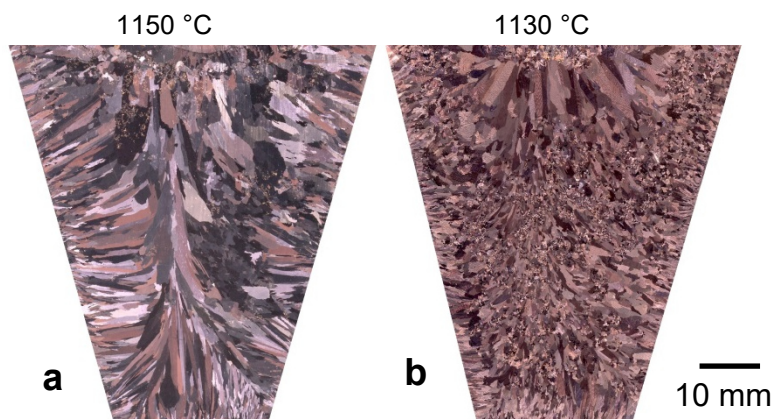
**Fig. 3** Grain structure of DHP-Cu: a) cast 5 of B (262B, 260P, 1150 °C) [5] and b) cast 6 of B+Ag (1130 °C)



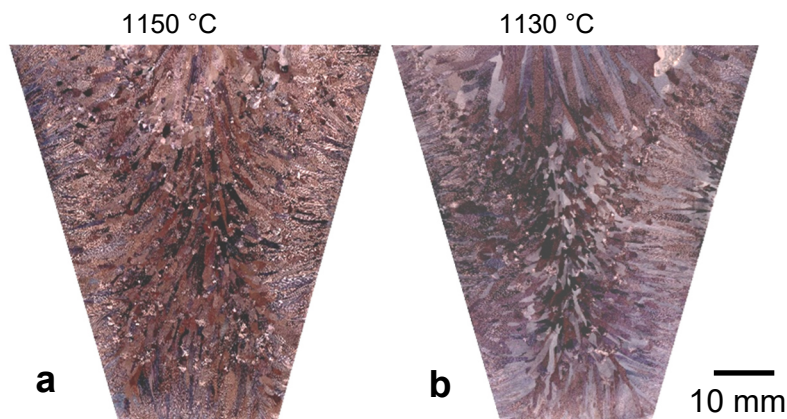
On decreasing the casting temperature from 1150 °C to 1130 °C, the grain structure changed from large, non-uniform columnar [cast 7 of Mg (**Fig. 4 a**), cast 9 of Ca (**Fig. 5 a**) and cast 13 of Zr (**Fig. 7 a**)] to some degree of CET with extremely coarse equiaxed grain sizes, for cast 8 of Mg+Ag (**Fig. 4 b**); to CET to a lesser extent compared with that of the DHP-Cu reference cast 4, for cast 10 of Ca+Ag (**Fig. 5 b**) and cast 14 of Zr+Ag (**Fig. 7 b**). **Fig. 5 b**) also indicates the greater variability in grain size seen in cast 10 of Ca+Ag at 1130 °C, i.e. pockets of small equiaxed grains surrounded by large columnar grains. Those results are also summarized in **Table 1**.



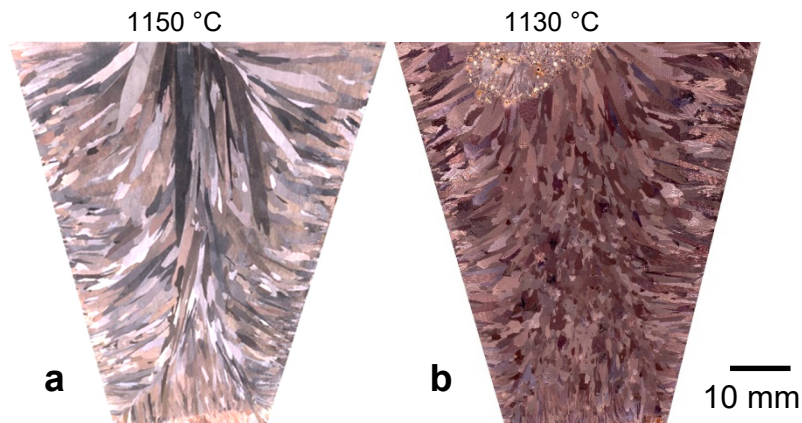
**Fig. 4** Grain structure of DHP-Cu: a) cast 7 of Mg (754Mg, 218P, 1150 °C) [5] and b) cast 8 of Mg+Ag (1130 °C)



**Fig. 5** Grain structure of DHP-Cu: a) cast 9 of Ca (448Ca, 264P, 1150 °C) [5] and b) cast 10 of Ca+Ag (1130 °C)



**Fig. 6** Grain structure of DHP-Cu: a) cast 11 of Ti (35Ti, 371P, 1150 °C) and b) cast 12 of Ti+Ag (1130 °C)



**Fig. 7** Grain structure of DHP-Cu: a) cast 13 of Zr (166Zr, 250P, 1150 °C) [5] and b) cast 14 of Zr+Ag (1130 °C)

**Table 1** Nominal and chemical compositions of investigated microalloying additions and macrostructure

Cast		T (°C)	Nominal compositions (wt.%)	ICP-OES trace analysis (wt.ppm)	Master alloys / materials (wt.%)	Macrostructure	Ref.
1		1150	0.039P	300P	Cu-15P	CET less. ext.	4
2		1130	0.039P			CET less. ext.	
3	Ag	1150	0.069P, 0.015Ag	396P, 143Ag	Ag (99.9)	CET less. ext.	4
4	Ag	1130	0.039P, 0.015Ag			CET	
5	B	1150	0.170B, 0.069P	262B, 260P	Cu-1.73B-0.04Si-0.01Fe- 0.01Sn-0.005Pb	CET exc. eq. gr. c.	5
6	B+Ag	1130	0.1B, 0.039P, 0.015Ag			CET exc. eq. gr. c.	
7	Mg	1150	0.085Mg, 0.030P	754Mg, 218P	Cu-20Mg	Large columnar	5
8	Mg+Ag	1130	0.1Mg, 0.039P, 0.015Ag			CET exc. eq. gr. c.	
9	Ca	1150	0.085Ca, 0.030P	448Ca, 264P	Cu-6.87Ca-0.005Al- 0.001Fe-0.001Mg	Large columnar	5
10	Ca+Ag	1130	0.1Ca, 0.039P, 0.015Ag			CET less. ext.	
11	Ti	1150	0.1Ti, 0.039P	35Ti, 371P	Cu-28.924Ti-0.045Fe- 0.09Fe-0.002Pb	CET less. ext.	
12	Ti+Ag	1130	0.1Ti, 0.039P, 0.015Ag			CET less. ext.	
13	Zr	1150	0.085Zr, 0.030P	166Zr, 250P	Cu-9.28Zr-0.11Sn- 0.09Fe-0.002Pb	Large columnar	5
14	Zr+Ag	1130	0.1Zr, 0.039P, 0.015Ag			CET less. ext.	

exc. eq. gr. c. – excessive equiaxed grain coarsening; less. ext. – to a lesser extent compared with that of the DHP-Cu reference cast 4; Note that, in general, casts at 1150°C were previously reported [4, 5]. New results are reported herein at 1130°C.

#### 4. CONCLUSION

The effects the combined addition of 0.039 wt.% P + 0.015 wt.% Ag as well as a nominal addition of 0.1 % of the de-embrittling elements of copper – B, Mg, Ca, Ti and Zr – on the grain size structure at a casting temperature of 1130 °C were determined and compared to those without the microalloying addition of 0.015% Ag obtained at a casting temperature of 1150 °C under TP-1 casting conditions:

1. On decreasing the casting temperature from 1150 °C to 1130 °C, the degree of CET increased for a given DHP-Cu reference composition.
2. The microalloying addition of Ag of 0.015 % to DHP-Cu was essential for grain size control.

3. In comparison to the corresponding DHP-Cu reference cast at 1150 °C and 1130 °C, no further grain refining action was observed due to B, Mg, Ca, Ti and Zr microalloying additions for the conditions studied.

## ACKNOWLEDGEMENTS

*The financial support from EPSRC and supply of pure Cu by Rautomead Ltd. are gratefully acknowledged.*

## REFERENCES

- [1] GALVAO I., LOUREIRO A., RODRIGUES D. M. Influence of process parameters on the mechanical enhancement of copper-DHP by FSP. *Advanced Materials Research*, Vol. 445, 2012, pp. 631-636.
- [2] BAGHERIAN E. R., BELL C., COOPER M., FAN Y., FRAME B., ABDOLVAND A. Influence of casting speed on the structure and mechanical properties of continuous cast DHP copper tube. In *METAL 2014: 23<sup>rd</sup> International Conference on Metallurgy and Materials*. Ostrava: TANGER, 2014, pp. 1163-1168.
- [3] New UPCAST® Developments target copper tube production and environmental benefits. *Technology News International*, Vol. 99, 2010, pp. 28-29.
- [4] BALART M. J., PATEL J. B., FAN Z. Grain refinement of DHP copper by particle inoculation. *International Journal of Cast Metals Research*, Vol. 28, No. 4, 2015, pp. 242-247.
- [5] BALART M. J., PATEL J. B., GAO F., FAN Z. Grain refinement of DHP copper by elemental additions. *International Journal of Cast Metals Research*, Vol. 28, No. 4, 2015, pp. 248-256.
- [6] DAVIS J. R. (ed.) *Copper and Copper Alloys*. ASM Speciality Handbook. 2<sup>nd</sup> edn. Materials Park, OH. ASM International, 2008, pp. 171-194.
- [7] LAPORTE V., MORTENSEN A. Intermediate temperature embrittlement of copper alloys. *International Materials Reviews*, Vol. 54, No. 2, 2009, pp. 94-116.
- [8] LÓPEZ A., MITTEMEIJER E. J. The solubility of C in solid Cu. *Scripta Materialia*, Vol. 51, 2004, pp. 1-5.
- [9] Standard test procedure for aluminum alloy grain refiners: TP-1. The Aluminum Association, Washington DC, 1987.