



# Effects of Superheat and Solute Additions on the Grain Size in Binary Copper Alloys

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## Abstract

By utilizing data from the literature, we examine the effects of superheat and solute additions on the grain size (as measured by columnar grain length) in binary copper alloys. Our investigation provides support for an Arrhenius-like behavior of the superheat on the grain size. We also find a correlation between the columnar grain length at a constant degree of superheat and the variation of the reciprocal of the *true* growth restriction factor ( $1/Q$ ) with P, Mg, Mn, Pb, and Sn solute additions to a power of law of  $1/3$ , which gave a better fit than a linear one.

**Keywords** Grain size · Growth restriction · Solidification · Copper alloys

## Introduction

Grain refinement of copper and copper alloys has recently attracted the interest of the scientific community [1–7]. It is worthwhile briefly highlighting previous studies on grain refinement in copper and copper alloys [8–13]: *in air*, in the late 1930s by Northcott [8, 9], and in a protective atmosphere of *pure Ar* (99.997 pct), in the early 1990s by Bustos and Reif [10–13].

Potent, efficient, and sufficient number of highly dispersed particles of a required size distribution and composition during solidification at large undercoolings are necessary conditions but not sufficient, as solute is also needed in the melt to restrict grain growth [14].

Since Easton and StJohn [15] first proposed the concept of thermodynamically determined  $Q$  from the initial slope

in the constitutional supercooling, it has been adapted by several researchers [16–18]. Quedest et al. [16] calculated  $Q$  values in the L +  $\alpha$  region for some hypothetical ternary Al–X1–X2 systems. Schmid-Fetzer and Kozlov [17] evaluated  $Q$  in multicomponent alloys.

$$Q_{\text{true}} = \left( \frac{\partial(\Delta T_{\text{cs}})}{\partial f_s} \right)_{f_s \rightarrow 0} \quad (1)$$

where  $\Delta T_{\text{cs}}$  is the constitutional undercooling and  $f_s$  is the solid fraction.

$Q$  reflects the phase diagram of the alloy system and has a relationship with grain size [17], which was empirically found in some cases to be linear, as illustrated with some examples from the literature for Mg [19, 20] and Al [21] alloys in Ref. [22], where  $Q$  values were calculated from the *conventional* relationship:

$$Q_{\text{conv.}} = mc_0(k - 1) \quad (2)$$

where  $m$  is the slope of the liquidus,  $c_0$  is the solute concentration, and  $k$  is the equilibrium distribution coefficient [5].

In the aforementioned study, Men and Fan [22] developed an analytical model for determining the effects of different solute additions on grain refinement under isothermal solidification. The grain size was found to be directly related to  $(1/Q_{\text{conv.}})^{1/3}$  through a parameter  $B$ , which is dependent on the diffusion coefficient of the solute in the liquid phase, undercooling, growth velocity, and solid fraction at the moment of recalescence—in that solute enrichment at the solid/liquid

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interface can reduce the growth velocity and can increase the maximum undercooling before recalescence.

$$d = B \left( \frac{1}{Q_{\text{conv.}}} \right)^{1/3} \tag{3}$$

where  $B$  is a constant independent of alloy composition. Equation 3 gave a better fit to the experimental data than a linear one for binary Al–Zn and Al–Si alloys as well as Al-based wrought alloys solidified under TP-1 casting conditions [22].

We have found it of interest to explore the efficacy of the 1/3 power law (Eq 3), but from the *true* growth restriction factor framework, in binary copper alloys. By using experimental data from Northcott’s work [9], the effect of solute additions on the grain size has been evaluated in binary copper alloys using the analytical model provided by Men and Fan [22] for constant and various degrees of superheat. Liquid superheat is one of the main factors controlling heat transfer phenomena and solidification in upcasting of copper and brass and hence fundamental to understanding and predicting heat extraction rates [23]. The *true* growth restriction factor  $Q_{\text{true}}$  has been calculated rigorously for binary Cu–X alloys, where X = Al, Zn, P, Mg, Mn, Ni, Pb, and Sn.

### Thermodynamically Determined Q

$Q_{\text{true}}$  was thermodynamically calculated for each amount of solute present in binary copper alloys using the methodology described by Cziegler and Schumacher [3] based on the procedure given by Schmid-Fetzer and Kozlov [17] as follows. The development of the solid fraction ( $f_s$ ) was calculated using the Scheil–Gulliver solidification equation generally for a temperature step of 0.01 °C, unless otherwise stated in Table 1. Software package Pandat (version 8.0) and the thermodynamic databases available in the literature [24–30] were used to calculate cooling.

$$\Delta T_{cs} = T_L - T \tag{4}$$

where  $T_L$  is the liquidus temperature.

$$\Delta T_{cs} = a + bf_s + cf_s^2 \tag{5}$$

The derivative of the second-order polynomial at  $f_s \rightarrow 0$  leads to  $Q_{\text{true}} = b$

It is of interest to note that, in the limit  $f_s \rightarrow 0$ , the *true* and *conventional* growth restriction factors are identical (see the derivation in Ref. [17]).

$$Q_{\text{true}} = \left( \frac{\partial(\Delta T_{cs})}{\partial f_s} \right)_{f_s \rightarrow 0} = mc_0(k - 1) = Q_{\text{conv.}} \tag{6}$$

In this work,  $Q$  refers to  $Q_{\text{true}}$ .

## Results and Discussion

### Superheat Effect

The effect of both cast at 1200 °C and at a constant superheat of 100 °C on the grain size (as measured by columnar grain length) in binary Cu–XAl alloys of Ref. 9, where X = 0.1–7 wt.%, is shown in Fig. 1a, from which it can be seen that the grain structure of the binary Cu–Al system is representative of a type of an unrestricted columnar grain growth (101.6 mm) due to a high thermal gradient from liquid to solid at  $1/Q \geq 10$  (1/K). This behavior is reflected in a low correlation coefficient of the 1/3 power law of Eq 3 (Fig. 1a). These results were confirmed again by an addition of 0.21% of Al–5Ti–1B grain refiner to deoxidized copper, cast at 1150 °C under TP-1 casting conditions—constant cooling rate of 3.5 K/s at the center of a cross section located 38 mm from the base of the TP-1 sample—as described in Ref. [5]. As a result, excessive coarsening occurred as shown in Fig. 1b.

Again, it is also worthwhile reiterating the earlier point on the effect of solidification conditions on the grain size. Therefore, in theory, when comparing grain sizes from different alloys, those should have been cast at the same degree of superheat. However, in practice, this is not always the case, as generally reported in the literature [31]. Bolzoni and Babu [31] investigated superheat effects in binary Al–XSi alloys, where X = 4–10 wt.%, while fitting the experimental data to the Arrhenius-like relation (Eqs 7–8) that associated the grain size variation ( $\Delta d$ ) to the inverse of the difference between superheat ( $\Delta T$ ) because solidification is a diffusive process.

$$\Delta d = Ae^{-\frac{E_a}{R\Delta T}} \tag{7}$$

where  $\Delta d$  is the corresponding change in the difference in grain size from an alloy cast at a constant temperature compared with that cast from a constant superheat;  $A$  is the pre-exponential constant;  $E_a$  is the activation energy; and  $R$  is the gas constant 8.3145 J/mol K.

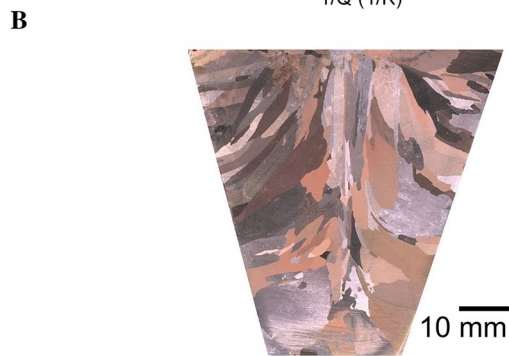
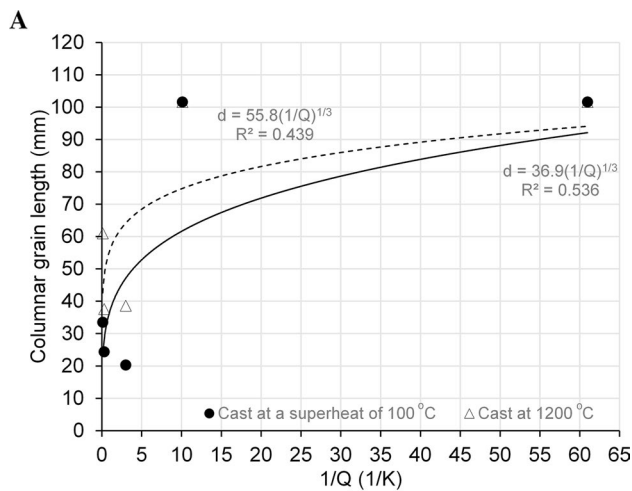
$$\ln(\Delta d) = \ln A - \frac{E_a}{R\Delta T} \tag{8}$$

The positive effect of decreasing the casting temperature (superheat) on grain size at two cooling rate conditions was highlighted in Ref. [10]. Northcott also observed this trend in his study [8] and reported that the average length of columnar grains decreased, from 20.32 to 12.7 mm for a binary Cu–0.5Sn alloy (in wt.%), on decreasing the superheat from 200 to 100 °C, and from 20.32 to 10.16 mm for a binary Cu–1Ca alloy (in wt.%), on decreasing the superheat from 140 to 10 °C. From Fig. 1a, the length of columnar grains decreased from 37.59 to 25.4 mm for Cu–5Al alloy ( $1/Q = 0.28$  1/K) and from 60.96 to 34.54 mm for Cu–7Al

**Table 1**  $Q$  for the binary Cu–X alloys calculated using the Scheil–Gulliver conditions for stable primary crystallization at different nominal compositions

Comp. (wt.%)	0.1	0.2	0.5	1	1	1	3	5	7	10	15	20	30	40
					Ref. [3] FactSage	Ref. [3] Thermo-Calc								
Al	$Q$ (K)	0.016		0.099	1.61 <sub>(5%)</sub>	–	0.334	3.565	8.365					
	fs	0.6087		0.1409			0.1011	0.1020	0.1003					
Zn	$T_{ss}$ (°C)								0.02					
	$Q$ (K)	0.054	0.493	0.983	1.03 <sub>(5%)</sub>	1.00 <sub>(5%)</sub>		4.971		15.00				
	fs	0.1074	0.1069	0.1000				0.1012		0.1002				
P	$T_{ss}$ (°C)													
	$Q$ (K)	1.949	3.983	10.622	23.510	23.48	56.647							
	fs	0.1012	0.1032	0.1009	0.1019		0.1024							
Mg	$T_{ss}$ (°C)		0.02	0.05	0.10		0.20							
	$Q$ (K)	2.503	15.679	34.122	30.05	29.33	70.417	100.470						
	fs	0.1004	0.1021	0.1019			0.1024	0.1040						
Mn	$T_{ss}$ (°C)			0.05	0.10									
	$Q$ (K)		2.429	4.846	4.86	5.27		21.082		29.972		21.479		
	fs		0.1050	0.1020				0.1013		0.1007		0.1030		
Ni	$T_{ss}$ (°C)			0.02	0.02			0.10		0.10		0.10		
	$Q$ (K)	0.376		3.540	3.52	3.53		15.226		26.479		43.682		53.741
	fs	0.1006		0.1018				0.1018		0.1021		0.1014		0.1014
Pb	$T_{ss}$ (°C)							0.05		0.10		0.20		0.20
	$Q$ (K)		0.706	1.768	3.452	2.59		13.494		40.934		64.344		
	fs		0.1015	0.1098	0.1010			0.1005		0.1001		0.1002		
Sn	$T_{ss}$ (°C)									0.10				
	$Q$ (K)		2.889	6.049	6.06	5.50	13.043	38.917		90.058				
	fs		0.0860	0.0699			0.1009	0.1004		0.1017				
	$T_{ss}$ (°C)			0.02			0.02	0.10		0.20				

 $f_s$  solid fraction $T_{ss}$  (°C) temperature step of 0.01 °C, unless otherwise stated



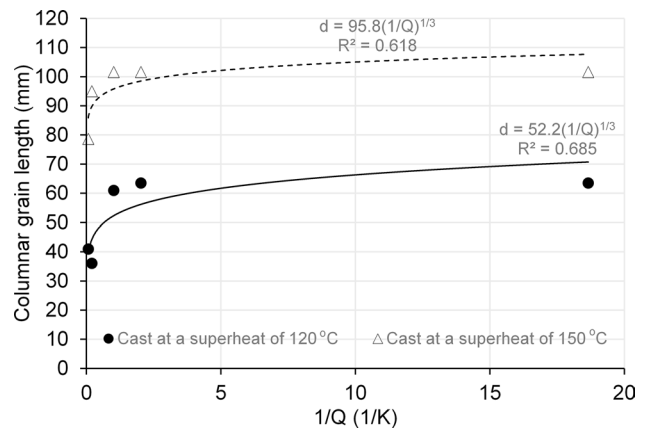
**Fig. 1** (a) Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu-XAl, where  $X=0.1-7$  wt.% and (b) macrograph of copper with an addition of 0.21% of Al-5Ti-1B grain refiner, cast at 1150 °C

alloy ( $1/Q=0.12$  1/K), when cast at 1200 °C to cast at a constant superheat of 100 °C, respectively. The  $A$  value obtained from Eq 8 is 89.56, and the  $E_a$  value is 474.7 J/mol.

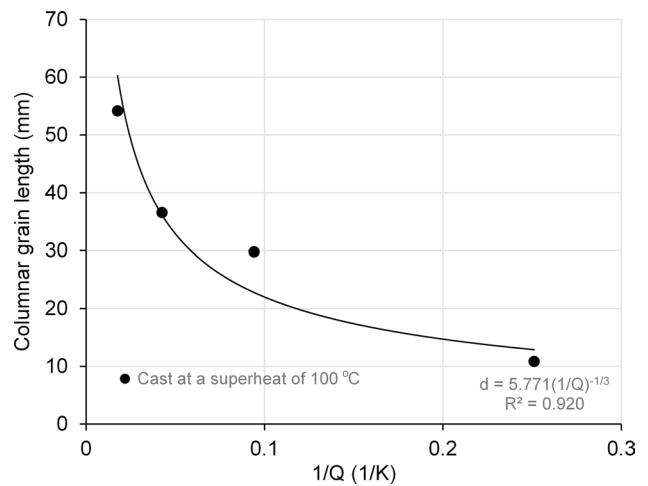
**Solutal Effect**

$Q$  values obtained in the present investigation are given in Table 1 as well as those of Ref. [3] obtained for a constant solute addition of 1% of Al, Zn, P, Mg, Mn, Ni, Pb, and Sn. From Table 1, it can be seen that similar  $Q$  values at 1% of solute addition were obtained when comparing FactSage and Thermo-Calc databases with those of this study. Columnar grain length values of Ref. [9] which were determined for additions into copper rapidly cast in air (~3.175 kg ingot castings, 76.2 mm diameter and ~76.2 mm height) are plotted against the corresponding calculated  $1/Q$  values using Eq 3 in Figs. 1a, 2, 3, 4, 5, 6, 7, and 8. The results were fitted to the  $1/3$  power law Eq 3. It can be seen that the  $1/3$  power law model can generally explain the experimental data for casts at a constant superheat.

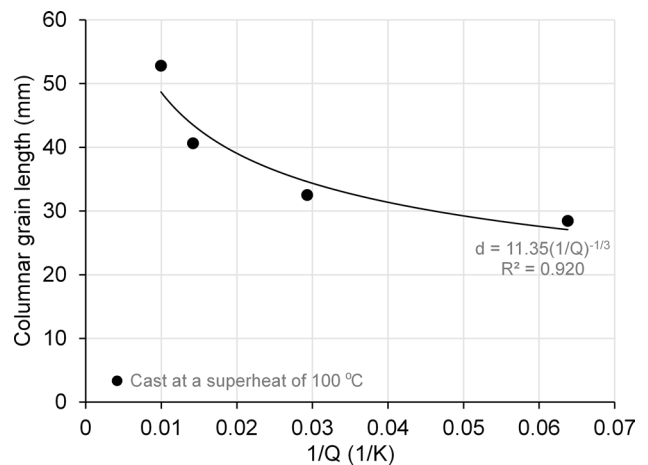
Zn has a rather high equilibrium vapor pressure which can be found in thermodynamic tables [32, 33]. As a result,



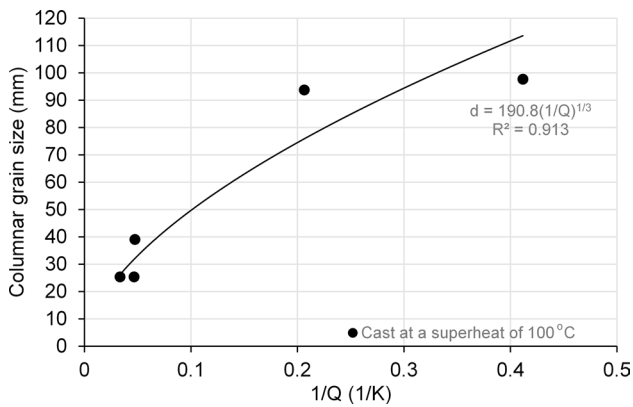
**Fig. 2** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu-XZn, where  $X=0.2-15$  wt.%



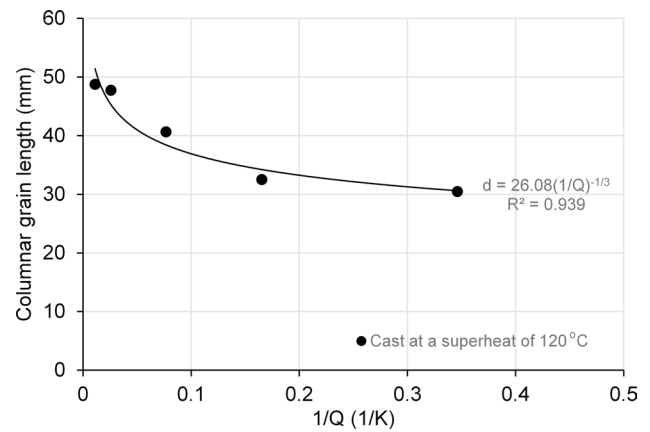
**Fig. 3** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu-XP, where  $X=0.1-2$  wt.%



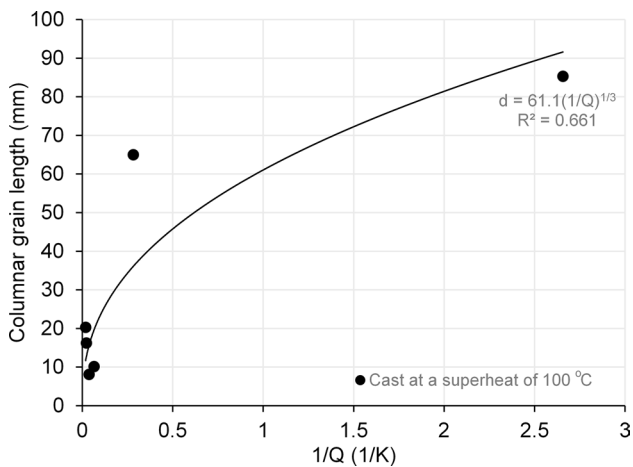
**Fig. 4** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu-XMg, where  $X=0.1-3$  wt.%



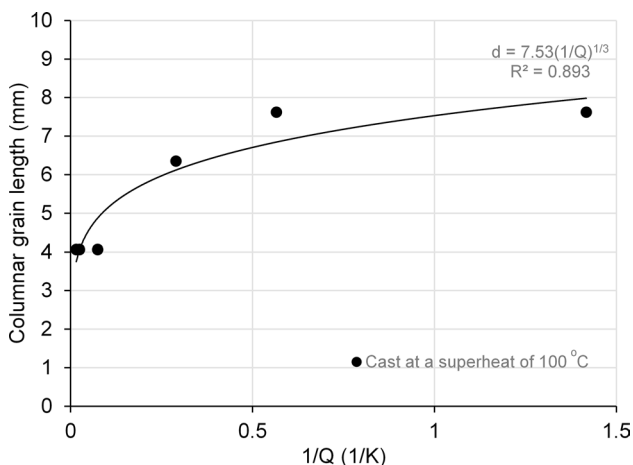
**Fig. 5** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu–XMn, where  $X=0.5\text{--}20$  wt. %



**Fig. 8** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu–XSn, where  $X=0.5\text{--}10$  wt. %



**Fig. 6** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu–XNi, where  $X=0.1\text{--}40$  wt. %



**Fig. 7** Variation of the average columnar grain length values [9] with growth restriction factor  $Q$  for Cu–XPb, where  $X=0.2\text{--}30$  wt. %

these Cu–Zn alloys would be expected to have a lower Zn content in the base composition than its corresponding nominal composition, which in turn may have resulted in a lower correlation coefficient of the  $1/3$  power law of Eq 3 (Fig. 2) compared with those of Figs. 3, 4, 5, 7, and 8. Those examples illustrate the need for consistency when comparing not only the superheat effect but also the solutal effect on the grain size of in copper alloys.

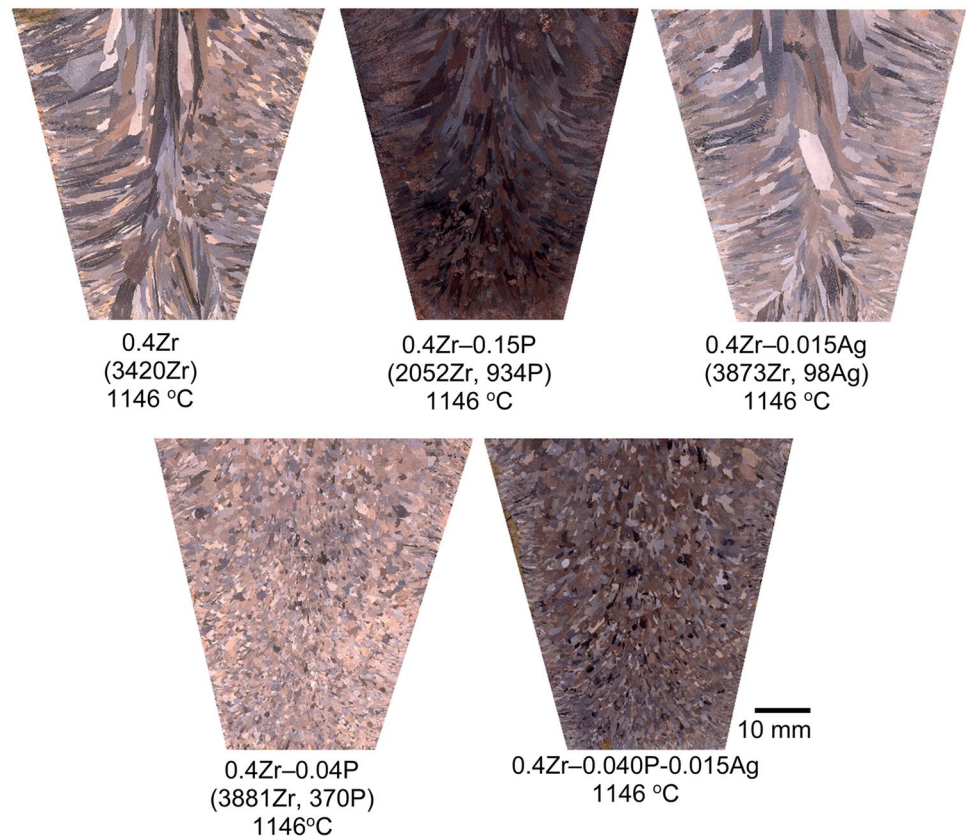
All that brings back to the point that both nucleating particles and solute additions are needed for effective grain refinement. This situation is qualitatively exemplified in Fig. 9, which shows (in wt. %) that 0.4Zr; 0.4Zr–0.15P; and 0.4Zr–0.015Ag alloys had a columnar grain structure, whereas 0.4Zr–0.04P and 0.4Zr–0.04P–0.015Ag alloys gave columnar-to-equiaxed transition (CET). The reason for variation in grain structure was ascribed to be due to the ease of nucleation [5] rather than only the effect of Zr additions of 0.4%.

## Conclusions

This study has examined the effect of superheat and solute additions on the grain size (as measured by columnar grain length) in copper alloys by utilizing data from the literature and by thermodynamically calculating the growth restriction factor for each amount of solute present in binary copper alloys.

An Arrhenius-like behavior has been exemplified for the corresponding change in the difference in grain size (columnar grain length) for solute additions of Cu–5Al and Cu–7Al (in wt. %) cast at 1200 °C compared with that cast from a constant superheat of 100 °C. It has also been found a correlation between the columnar grain length at a constant degree of superheat and the variation of the

**Fig. 9** Macrographs of Cu–0.4Zr, Cu–0.4Zr–0.15P, Cu–0.4Zr–0.015Ag, and Cu–0.4Zr–0.04P–0.015Ag alloys (in wt.%). Chemical compositions by ICP-OES (in wt ppm) and casting temperatures are shown for each TP-1 sample [5]



reciprocal of the *true* growth restriction factor ( $1/Q$ ) with P, Mg, Mn, Pb, and Sn solute additions to be a power of law of  $1/3$ , which gave a better fit than a linear one.

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