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TECHNICAL ARTICLE

On the Role of Dilute Solute Additions on Growth Restriction in Binary Copper Alloys

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Abstract
The effect of dilute solute additions on growth restriction in binary Cu alloys has been assessed at different degrees of superheat. Columnar grain length values from Northcott's work (Northcott in J Inst Metals 62:101-136, 1938) for binary Cu alloys were plotted against the corresponding undercooling parameter (P), the reciprocal of the *conventional* ($Q_{conv.}$) and *true* (Q_{true}) growth restriction factor (Schmid-Fetzer and Kozlov in Acta Mater 59(15):6133-6144, 2011) values. It was found that there was no correlation between the columnar grain length values and P, $1/Q_{conv.}$ and $1/Q_{true}$ values for different solutes and cast at the same degree of superheat. Unlike P, $Q_{conv.}$, and Q_{true} values, the heuristic growth restriction parameter (β) (Fan et al. in Acta Mater 152, 248-257, 2018) modeling framework in conjunction with the critical solute content (C^*) for growth restriction fitted well to binary Cu alloys.

Keywords Grain size · Supercooling parameter · Growth restriction factor · Growth restriction parameter · Solidification · Undercooling · Copper alloys

Introduction

In line with investigations on the effect of solute additions on the grain size in copper, growth restriction factors (Q) have been determined as exemplified by means of the *conventional* (Eq. 1) [4–7] or *true* (Eq. 2) [2, 8, 9] Q values to quantify the potential restriction to growth imposed by a solute. The *conventional* Q was expanded to multicomponent systems but disregarding solute-solute interactions, in which the *true* Q accounts for [8].

$$Q_{conv.} = mC_O(k-1) \tag{1}$$

where m is the slope of the liquidus, C_O is the solute concentration, and k is the equilibrium distribution coefficient. Equation 1 captures the phase diagram of the alloy system. Therefore, the accuracy of the *conventional* Q depends not only on solute-solute interactions, but also on the resolution of the binary phase diagram [8] and the values of k and m, which are not expected to be constant as they can vary with alloy composition and temperature [8, 10].

$$Q_{true} = \left(\frac{\partial(\Delta T_{cs})}{\partial f_s}\right)_{f_s \to 0} \tag{2}$$

where ΔT_{cs} is the constitutional undercooling and f_s is the solid fraction.

$$\Delta T_{cs} = T_L - T \tag{3}$$

where T_L is the liquidus temperature

Q_{true} was thermodynamically-calculated for each amount of solute present in binary copper alloys by relating ΔT_{cs} to the solid fraction (f_s) as described by Cziegler and Schumacher [8]:

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$$\Delta T_{cs} = a + bf_s + cf_s^2 \tag{4}$$

and linking to the Q_{true} Eq. (2) as derived by Schmid-Fetzer and Kozlov [2]. It follows that the derivative of second-order polynomial at $f_s \rightarrow 0$ (Eq. 4), leads to $Q_{true} = b$

Another parameter proposed for evaluating the effect of solute additions on grain refinement, for example in Al alloys, has been the constitutional supercooling parameter (P) [9]. Its accuracy is also dependent on the accuracy of k and m values.

$$P = \frac{mC_O(k-1)}{k} \tag{5}$$

Men and Fan [11] have highlighted, based on previously reported experimental results, that a simple linear relationship between grain size and growth restriction factor cannot hold in some cases. In their work [11], they developed theoretically and proved empirically a correlation between grain size and the reciprocal of the *conventional* growth restriction factor to be a power of law of 1/3. This was subsequently adapted to the *true* growth restriction factor on a study of the effects of superheat and solute additions of Al, Zn, P, Mg, Mn, Ni, Pb, and Sn on the grain size at a constant degree of superheat in binary copper alloys [12]. This paper extends our previous study to other binary copper alloys.

More recently, Fan *et al.* [3] defined the new growth restriction parameter (β):

$$\beta = \frac{mC_O(k-1)}{\Delta T} - k = \frac{Q_{conv.}}{\Delta T} - k \tag{6}$$

where ΔT is a fixed undercooling during solidification.

It is of interest to note that by replacing $\Delta T = m(C_O - C_L)$ and $k = C_S/C_L$ into Eq. 6, Fan *et al.* [3] obtained the heuristic solution for the accurate calculation of β values for a binary system (Eq. 7), which extended to multicomponent systems by the linear addition of each binary system β_i (Eq. 8) assuming no interactions between solutes.

$$\beta = \frac{C_O - C_S}{C_L - C_O} = \frac{f_L}{f_S} \tag{7}$$

$$\beta = \sum_{i=1}^{n} \beta_i \tag{8}$$

For eutectic systems, $k < 1$, then the difference between β calculated from Eq. 6 and that calculated from Eq. 7 is small and Eq. 6 is a good estimate of values of β. However, for peritectic systems, $k > 1$, such difference is larger and the calculation of β from the ratio of liquid to solid fraction (Eq. 7) is more accurate [3].

It was also derived in Ref. [3], the growth restriction coefficient ($2/\lambda^2$, (Eq. 9)), which applies for spherical growth during solidification.

$$\frac{2}{\lambda^2} = \frac{1-\alpha}{\alpha\left(1+\sqrt{\alpha}+\alpha\right)} \tag{9}$$

As well as the relationship between β and the solute supersaturation (α)

$$\alpha = \frac{1}{\beta + 1} \tag{10}$$

Critical solute concentrations are calculated by Eq. 11, which was obtained by rearranging Eq. 6 at $\beta = 0$.

$$C^* = \frac{k\Delta T}{m(k-1)} \tag{11}$$

Physically, C^* is the critical solute concentration for the onset of growth restriction [3], i.e., for a given undercooling:

if $C_O < C^*$, there is no growth restriction,

if $C_O > C^*$, there is growth restriction, the degree of which increased with increasing solute concentration.

We also update the earlier calculations [5] to take into account the heuristic β.

Previous studies have shown a low correlation between $Q_{conv.}$ [4–6] and Q_{true} [8] values and grain size in binary Cu alloys. Plots of the variation of grain size values with $Q_{conv.}$ were reported for many binary Cu alloys in the former studies [4–6], however, only for P, Zr, and Ni in the latter study [8]. Here, we report columnar grain length values from Northcott's work [1] for binary Cu alloys plotted against the undercooling parameter (P), the reciprocal of the *conventional* growth restriction factor ($Q_{conv.}$) values and the reciprocal of the *true* growth restriction factor (Q_{true}) [2] values for different solutes and cast at different degrees of superheat. Furthermore, the heuristic growth restriction parameter (β) [3] modeling framework in conjunction with the critical solute content (C^*) for growth restriction has also been applied to binary Cu alloys. This work has been undertaken to compare and contrast the three different factors, namely P, $Q_{conv.}$ and Q_{true} and the holistic parameter β in conjunction with the critical solute content (C^*) for growth restriction in predicting the grain size in binary copper alloys. *A priori*, β is expected to give a better fit than that of others.

True Growth Restriction Factor Q

The *true* growth restriction factor Q was thermodynamically-calculated for each amount of solute present in binary copper alloys using the methodology described by Cziegler and Schumacher [8] based on the original Schmid-Fetzer

Table 1 Q_{true} for the binary Cu-X alloys calculated from the Gulliver-Scheil cooling conditions using Pandat for stable primary crystallization in the range 0.1–10 wt.%, where columnar grain length values are provided in the original publication [1]

Comp. (wt.%)		0.1	0.2	0.5	1	1 Ref. [8] FactSage	1 Ref. [8] Thermo-Calc	2	3	5	7	10	C^* $\Delta T = 0.2\ K$	C^* $\Delta T = 0.5\ K$	System
Nb	Q (K)					$87.52_{(0.1\%)}$	$84.70_{(0.1\%)}$						0.010	0.026	Peritectic
B	Q (K)						19.58						0.000	0.001	Eutectic
O	Q (K)					$38.02_{(0.2\%)}$							0.000	0.000	Eutectic / monotectic
Mg [12]	Q (K)	2.503		15.679	34.122	30.05	29.33	70.417	100.47				0.001	0.001	Eutectic
	f_s	0.1004		0.1021	0.1019			0.1024	0.1040						
	T_{ss} (K)			0.05	0.10			0.25	0.5						
S	Q (K)			2.477		$28.29_{(0.5\%)}$							0	0	Eutectic
	f_s			0.1074											
P [12]	Q (K)	1.949	3.983	10.622	23.510	23.48	27.03	56.647					0.001	0.002	Eutectic,
	f_s	0.1012	0.1032	0.1009	0.1019			0.1024							Congruent
	T_{ss} (K)		0.02	0.05	0.10			0.20							
Ca	Q (K)			9.974	21.693	18.43	21.43	49.656					0	0	Eutectic
	f_s			0.1022	0.1017			0.1024							
	T_{ss} (K)			0.05	0.10			0.20							
Tl	Q (K)				3.547	3.34							0.001	0.001	Monotectic
	f_s				0.1008										
Si	Q (K)			4.499	8.535	11.28	9.53	20.917					0.006	0.015	Peritectic
	f_s			0.1018	0.1001			0.1010							
	T_{ss} (K)				0.02			0.05							
Se							8.82						0	0	Monotectic
Y						9.44							0	0	Eutectic
Zr	Q (K)				8.3181	8.39	8.37						0	0	Eutectic
	f_s				0.1006										
	T_{ss} (K)				0.02										
Ti	Q (K)	0.906		4.352	8.661	8.69	8.70	17.188					0.006	0.015	Intermediate
	f_s	0.1034		0.1038	0.1042			0.1003							Solid solution
	T_{ss} (K)			0.02	0.05			0.1							Phases / compounds
Sr						8.37							0	0	Intermediate compounds
Sn [12]	Q (K)			2.889	6.049	6.06	5.50	13.043		38.917		90.058	0.002	0.006	Peritectic
	f_s			0.0860	0.0699			0.1009		0.1004		0.1017			
	T_{ss} (K)				0.02			0.02		0.10		0.20			
Mn [12]	Q (K)			2.429	4.846	4.86	5.27			21.082		29.972	0.015	0.038	Miscibility
	f_s			0.1050	0.1020					0.1013		0.1007			Gap in the
	T_{ss} (K)			0.02	0.02					0.10		0.10			Solid state

Table 1 (continued)

Comp. (wt.%)		0.1	0.2	0.5	1	1 Ref. [8] FactSage	1 Ref. [8] Thermo-Calc	2	3	5	7	10	C^* $\Delta T = 0.2\ K$	C^* $\Delta T = 0.5\ K$	System
Sb	Q (K)				5.560	4.96		11.738					0.006	0.015	Eutectic,
	f_s				0.1026			0.1023							Congruent
	T_{ss} (K)				0.02			0.05							
Mo	Q (K)			42620	10885								0.009	0.023	Peritectic
	f_s			0.0026	0.0059										
	T_{ss} (K)			0.5	1										
In	Q (K)				3.9754	4.39							0.009	0.023	Peritectic
	f_s				0.1001										
Ni [12]	Q (K)	0.376			3.540	3.52	3.53			15.226		26.479	0.081	0.203	Isomorphous
	f_s	0.1006			0.1018					0.1018		0.1021			
	T_{ss} (K)									0.05		0.10			
Bi	Q (K)					3.49	3.53	6.888					0	0	Very low
	f_s							0.1012							Solubility of
	T_{ss} (K)							0.02							Bi in Cu
Ag	Q (K)			1.746	3.497	3.51	3.54						0.014	0.036	Eutectic
	f_s			0.1011	0.1012										
Cr	Q (K)			2.775	5.393	3.45							0.029	0.073	Eutectic
	f_s			0.1003	0.1016										
	T_{ss} (K)				0.02										
Pb [12]	Q (K)		0.706	1.768	3.452	2.59	3.25			13.494			0.010	0.025	Monotectic
	f_s		0.1015	0.1098	0.1010					0.1005					
Fe	Q (K)	0.2004		1.017	1.884	1.19		3.276					0.126	0.314	Peritectic
	f_s	0.1008		0.1005	0.1024			0.1055							
	T_{ss} (K)							0.02							
Au	Q (K)	1.015				0.95	0.91						0.098	0.246	Miscibility
	f_s	0.1025													Gap in the solid state
Zn [12]	Q (K)		*0.054*	0.493	0.983	$1.03_{(5\%)}$	$1.00_{(5\%)}$			4.971			*0.155*	0.387	Peritectic
	f_s		0.1074	0.1069	0.1000					0.1012					
V	Q (K)				1652.9								0.383	0.958	Peritectic
	f_s				0.0113										
	T_{ss} (K)				1										
Al [12]	Q (K)	*0.016*			*0.099*	$1.61_{(5\%)}$	-	*0.334*		3.565	8.365		*2.040*	5.100	Intermediate
	f_s	0.6087			0.1409			0.1011		0.1020	0.1003				Solid solution phases

Table 1 (continued)

Comp. (wt.%)		0.1	0.2	0.5	1	1 Ref. [8] FactSage	1 Ref. [8] Thermo-Calc	2	3	5	7	10	C^* $\Delta T = 0.2\ K$	C^* $\Delta T = 0.5\ K$	System
Co	Q (K)				6.085	1.26									
	f_s				0.1030										
	T_{ss} (K)				0.02										
Cd							5.30								
Ba						5.40									
Ce	Q (K)			2.740		5.78									Eutectic
	f_s			0.1007											

Composition is listed across the top row, for various solute atoms which as listed down the first column. Critical solute content (C^*) for growth restriction is determined at undercoolings of 0.2 *K* and 0.5 *K*. Q_{true} values calculated from solute concentrations lower $C_O < C^*$ at ΔT of 0.2 *K*, are both marked with italics in the Zn and Al rows.

f_s solid fraction.

T_{ss} (*K*) temperature step of 0.01 *K*, unless otherwise stated.

and Kozlov's work [2]. This procedure was briefly described in our previous work [12]. Cooling was calculated from the thermodynamic databases available in the literature using Software package Pandat (version 8.0) following a compilation of Refs. [13–19] as cited in our previous work [12] and an extension to other binary copper alloys [20–40]. The solid fraction evolution within a relatively small fraction (f_s) as detailed in Table 1 was calculated based on the Gulliver-Scheil cooling conditions generally for a temperature step of 0.01K, except where otherwise stated in Table 1.

Growth Restriction Parameter β

Values of m and k were calculated and reported in Ref. [5] from which $Q_{conv.}$ values were determined in the present investigation. β defined from Eq. 6 was evaluated at a constant ΔT value of 0.2 *K*. α was calculated from the relationship with β (Eq. 10) obtained by Fan *et al.* [3] for calculating subsequently values of $2/\lambda^2$ using Eq. 9.

Results and Discussion

Q_{true} values calculated at a solute content of 1 wt.% of Ref. [8] and those calculated at different solute concentrations are compared in Table 1. In the latter case, columnar grain length values of Ref. [1], are plotted against the P, reciprocal of the $Q_{conv.}$ and Q_{true} values for different solutes and degrees of superheat in Fig. 1. Note that, columnar grain length values of Ref. [1] were assessed for additions into copper rapidly cast in air (~3.175 kg ingot castings, 76.2 mm diameter and ~76.2 mm height). Unrestricted type of columnar grain growth can occur under high thermal gradient (from liquid to solid).

Despite of the fact that a direct relationship between the columnar grain size and the reciprocal of the *true* growth restriction factor at a constant degree of superheat was found to be of a power of law of 1/3 for individual solute additions of P, Mg, Mn, Pb, and Sn [12], which were also included in Fig. 1; there was no correlation between columnar grain length values from Northcott's work [1] and the P, $1/Q_{conv.}$ and $1/Q_{true}$ values for different solutes and cast at the same degree of superheat. This is because it is expected that similar P, $1/Q_{conv.}$, and $1/Q_{true}$ values would give similar grain size values under the same casting conditions, independently of the alloy system. Relatively higher P and lower both $1/Q_{conv.}$ and $1/Q_{true}$ values would be expected to correlate highly with finer grain sizes. This is however not the case in Fig. 1. In the work from which Eq. (2) was derived [2], it has been highlighted that Q_{true} is identical to $Q_{conv.}$ in the limit $f_s \rightarrow 0$.

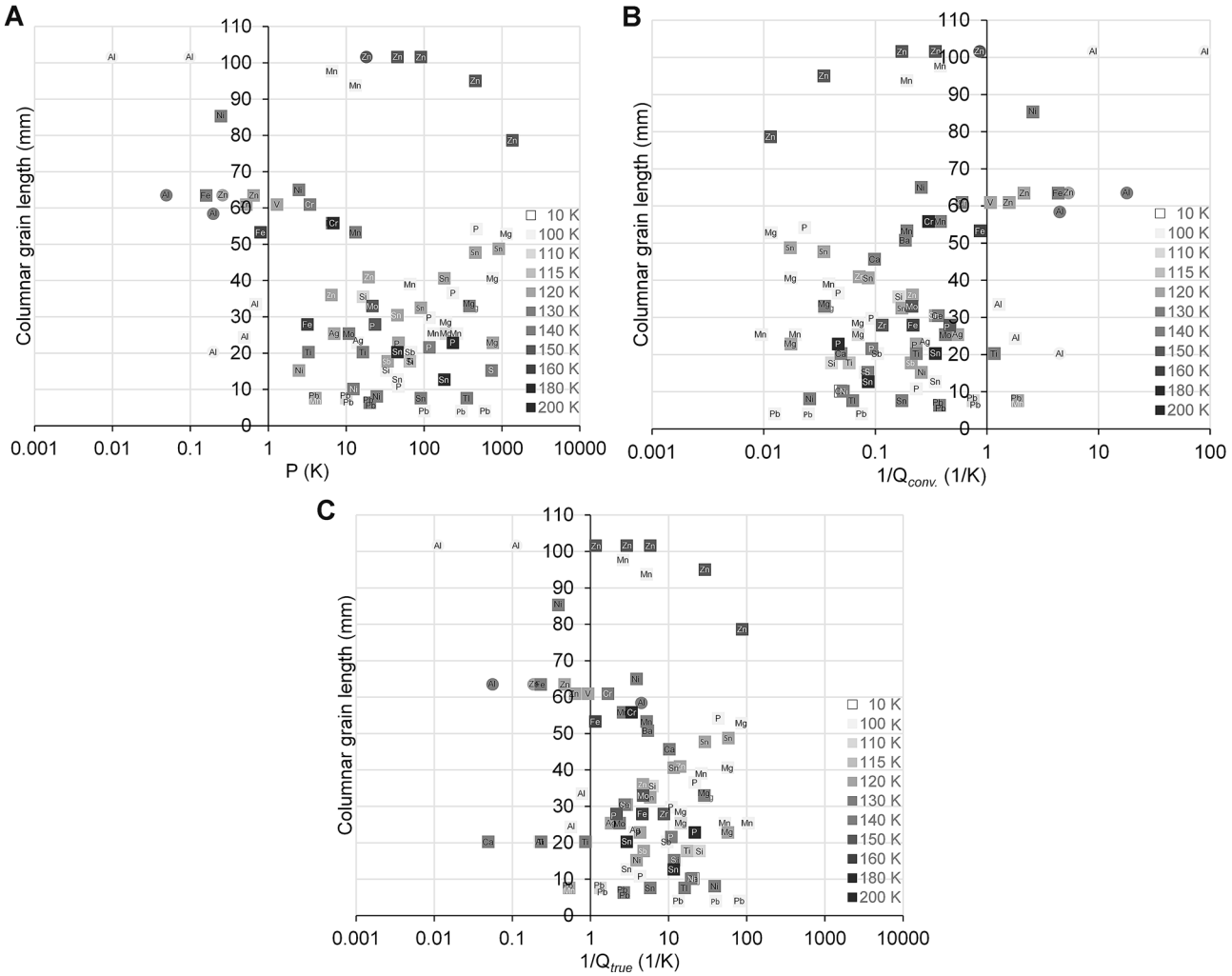

Fig 1 Variation of columnar grain length values of Ref. [1] with (**a**) P, and the reciprocal of (**b**) $Q_{conv.}$ and (**c**) Q_{true} values for different solutes and degrees of superheat.

Values of C^* at ΔT of 0.2 K and 0.5 K are given in Table 1. Q_{true} values calculated from solute concentrations lower $C_O < C^*$ at ΔT of 0.2 K, are both marked with italics in the Zn and Al rows in Table 1 and with circle symbols in Fig. 1. Interestingly, those points generally correspond to Zn and Al lying on the top, right hand side corner of the graph, where coarse columnar grains are represented, except for an Al point and a Zn point, in which case and as mentioned in Ref. [12] due to its inherent high equilibrium vapor pressure, these Cu-Zn alloys could have had a lower Zn content in the base composition than its corresponding nominal composition, which in turn may have resulted in an overestimation of the Q_{true} values.

Next, from the viewpoint of the new growth restriction modeling framework [3], $2/\lambda^2$ values are correspondingly represented against the ratio of $Q_{conv.}$ to ΔT in Fig. 2 and β values in Fig. 3. Note that, from Fig. 2, the intercept at the $Q_{conv.}/\Delta T$ corresponds to k as highlighted in the work from which Eq. 6 was derived by Fan *et al.* [3]. Finally, from Fig. 3, a direct relationship between $2/\lambda^2$ and β values has been found in this work in binary copper alloys, in agreement with results originally reported by Fan *et al.* [3].

Conclusions

The undercooling parameter, P, *conventional* $Q_{conv.}$ and *true* Q_{true} growth restriction factors as well as the heuristic growth restriction parameter (β) modeling frameworks have been applied to binary Cu alloys. There was no correlation between columnar grain length values from Northcott's work [1] and the P, reciprocal of the $Q_{conv.}$ and Q_{true} values for different solutes and cast at the same degree of superheat. Unlike P, $Q_{conv.}$, and Q_{true} values, the heuristic

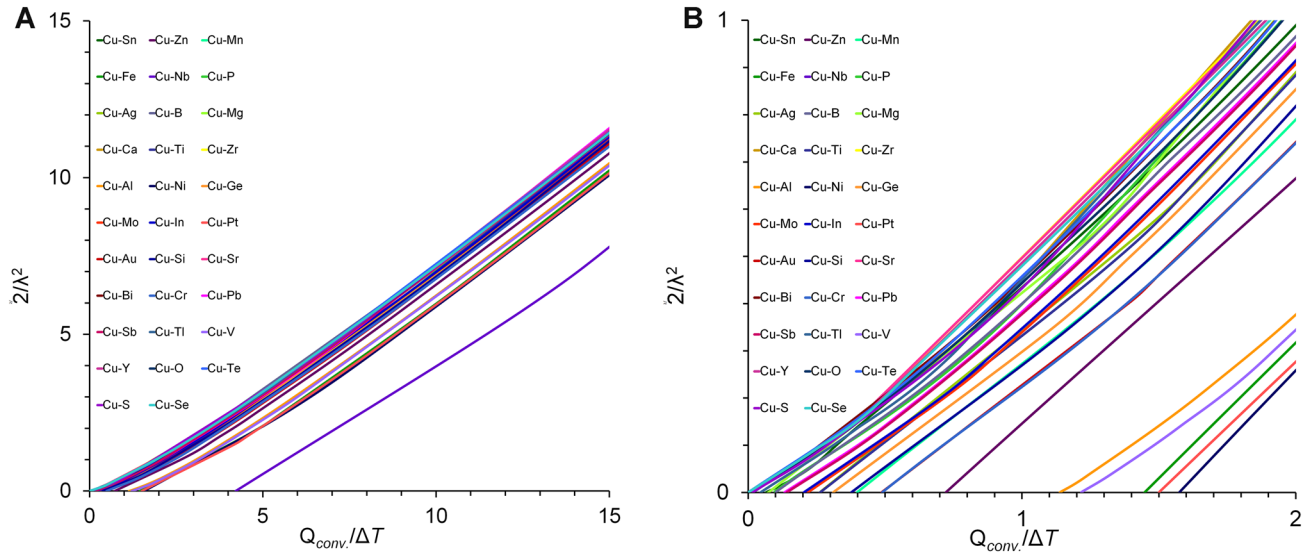

Fig 2 (**a**) Variation of $2/\lambda^2$ values with the ratio of $Q_{conv.}$ to ΔT at $\Delta T = 0.2\ K$ for binary copper alloys and (**b**) detailed region.

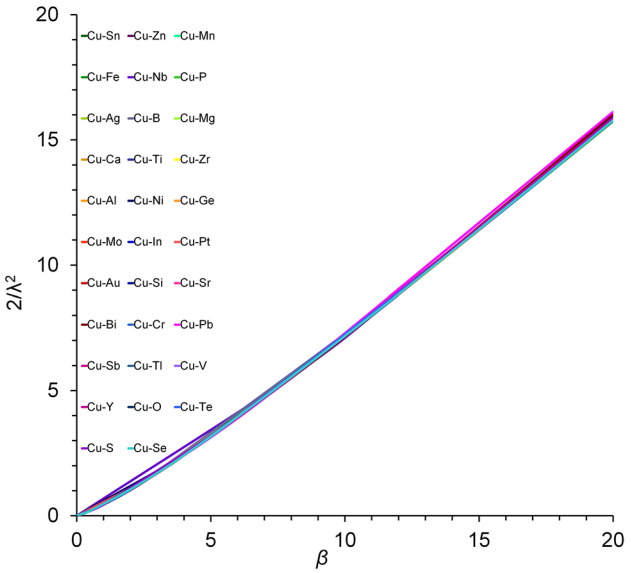

Fig 3 Variation of $2/\lambda^2$ values with β at $\Delta T = 0.2\ K$ for binary copper alloys.

growth restriction parameter (β) [3] modeling framework in conjunction with the critical solute content (C^*) for growth restriction fitted well to binary Cu alloys. Based on the latter analysis, a direct relationship between the growth restriction coefficient ($2/\lambda^2$) and the heuristic growth restriction parameter (β) was found in this work in dilute binary copper alloys. As concluded in Ref. [3], this means that growth velocity is a unique function of the growth restriction parameter (β), which is dependent on the nature of solutes, solute concentrations and solidification conditions. However, growth velocity is not a unique function of P, $Q_{conv.}$, and Q_{true} values.

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