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GROWTH LAW FOR COLUMNAR STRUCTURE WITHIN THE COPPER AND COPPER ALLOYS SOLIDIFYING AT A HIGH PECELET NUMBER

The copper and copper alloys' ingots have been subjected to structural observation in order to estimate the Peclet Number at which these ingots were solidifying. It was stated that the formation of columnar structure within the ingots occurred at a high Peclet Number, higher than the threshold value of this parameter, $Pe = 500$. The formulated relationships of the Growth Law correspond to a high Peclet Number due to application of the adequate development in series of the Ivantsov's function. The Growth Law has been developed on the basis of the definition of the wavelength of perturbation which leads to the dispersion of the planar s/l interface. New definition of the index of stability connected with the behavior of solute concentration at the s/l interface has been delivered. The current definition is related to non-equilibrium solidification. The index can be easily calculated using some parameters delivered by a given Cu-X phase diagram. Physical meaning of the formulated Growth Law has also been presented.

Keywords: Continuously cast copper ingots; Perturbation wavelength; Criterion of marginal stability

Symbols used in the text

- C – solute concentration,
- C_E – solute concentration at the eutectic point,
- C_0 – nominal solute concentration of an alloy,
- C_L^* – current solute concentration along liquidus line,
- C_S^* – current solute concentration along solidus line,
- D – diffusion coefficient in the liquid,
- G – thermal gradient at the columnar grain tip,
- G_C – concentration gradient at the columnar grain tip,
- m_L – slope of the liquidus line of a given phase diagram,
- Pe – Peclet Number,
- v – velocity of the liquidus isotherm movement,
- v_C – solidification rate for the columnar structure formation,
- $R_{exp.}$ – value of the tip radius resulting from the experiment,
- $R_{th.}$ – tip radius of the columnar grain as predicted theoretically,
- \hat{R} – average tip radius as measured/predicted within the structure,
- ΔS – entropy of fusion of a given alloy/phase,
- ΔT – undercooling of the moving s/l interface,
- ΔT_0 – temperature range for the equilibrium solidification,
- ΔT_N – temperature range for the non-equilibrium solidification,
- γ – surface tension,

- Γ – Gibbs-Thomson parameter of capillarity, $\Gamma = \gamma/\Delta S$,
- λ_S – wavelength of the perturbation created at the formerly existing planar s/l interface,
- ξ – index of the s/l interface stability resulting from the behavior of solute concentration,
- Ω – solute supersaturation.

1. Introduction

Columnar structure formation is usually observed as a dominant phenomenon which occurs during solidification of copper and copper alloys in such an industrial product like: ingot (Fig. 1a), strand (Fig. 1b), or rod (Fig. 1c).

The formation of columnar structure is governed by the constrained conditions of growth, that is by a steep positive thermal gradient and some diffusion phenomena occurring at the solid/liquid (s/l) interface, [1]. The latent heat is transported through the solid and heat flux is directed towards crystallizer surface while the solute is rejected at the s/l interface, [2].

The constant pulling rate of an ingot, band or rod through the appropriate crystallizer together with the geometry of a given system for solidification, both decide on the solidification rate

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Fig. 1a. Columnar structure revealed within the oxygen-free copper ingot / slice (295 mm in diameter); source: KGHM Polska Miedź S.A. – Copper Smelter “Legnica”



Fig. 1b. Exclusively columnar structure revealed within the copper strand (120 mm × 60 mm); source: KGHM Polska Miedź S.A. – Copper Smelter “Cedynia”

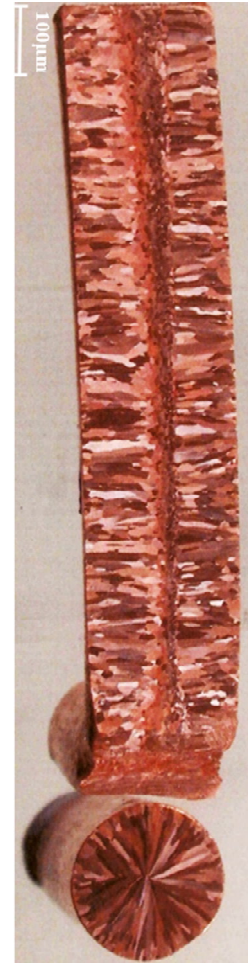


Fig. 1c. Columnar structure revealed within the copper rods (8 mm in diameter); The equiaxed structure along the rods’ axis is visible; source: KGHM Polska Miedź S.A. – Copper Smelter “Cedynia”

of the columnar structure and finally on the structure spacing. At first, however, the tip radius of columnar cell or dendrite is forming and eventually its value decides on the structure spacing, [3]. It is substantiated, because the solidification occurs under steady conditions during continuously cast alloys (the initial transient period of the process under investigation, is not taken into account, [4]). Finally, some relationships can be formulated as an adequate polynomial (named as the Growth Law) which relates the tip radius with the solidification rate.

Formulation of the mentioned polynomial should be preceded by the application of a criterion mathematically justified in the theory of solidification, [2]. In some situations the condition of minimum undercooling is treated as an optimization criterion, $\Delta T = \min.$, [5]. However, this condition has an intuitive character only, and is not justified mathematically. So, its application is limited.

On the other hand, the use of criterion of minimum entropy production which is justified mathematically (by the *Liouville*’ theorem) is complicated and the criterion is applicable to some solidification processes occurring strictly under steady state, [6].

Therefore, in the case of columnar structure formation it is justified to apply the so-called criterion of marginal stability,

determined by some numerical treatment connected with the dispersion of the initially created planar s/l interface, [7]. According to this criterion the tip radius of a columnar grain is equal to the perturbation wavelength which is responsible for the mentioned dispersion of the planar s/l interface, Eq. (1).

$$R_{th.} = \lambda_S \quad (1)$$

where the definition of the perturbation wavelength is as follows, [7]:

$$\lambda_S = 2\pi \cdot \left(\frac{\Gamma}{m_L \cdot \xi \cdot G_C - G} \right)^{0.5} \quad (2)$$

The ξ – parameter plays an essential role in Eq. (2) as well as in the behavior of the s/l interface stability perturbed by some possible fluctuations of the solute concentration. However, usually its definition is supposed to simplification in the theory of solidification, [2].

According to the mentioned simplification it is assumed that ξ – value is equal to unity, Eq. (3).

$$\xi = 1 \quad (3)$$

Consequently, the applied simplification results in the non-physical value of the p – partition ratio, it means, that the partition ratio becomes equal to zero, [2], Eq. (4).

$$p = 0 \quad (4)$$

The partition ratio defines the location of the liquidus and solidus lines in the phase diagram and the application of the Eq. (4) drastically changes the mentioned position of the solidus line. It is unacceptable from the thermodynamic viewpoint. Moreover, it makes the Growth Law to be erroneous when this polynomial is supposed / exploit to the theoretical prediction of the R_{th} – parameter (tip radius).

The current model makes attempt to show how the Growth Law could be formulated in relation to an adequate value of the Peclet Number estimated for the copper and copper alloys and first of all, how to eliminate unacceptable simplification imposed by Eq. (3), and Eq. (4).

2. Estimation of the Peclet Number

Definition of the Peclet Number for the columnar structure formation is:

$$Pe = \frac{R_{exp} \cdot v_C}{2D} \quad (5)$$

It is evident that the R_{exp} – parameter can be estimated within the columnar structure like this shown in Fig. 1. It allows to state whether the value of the Peclet Number is lower or higher than the threshold $Pe = 500$. When the Peclet Number values are higher than $Pe = 500$, then solidification is considered as that occurring at high values of the Peclet Number, [8].

The measurement of the tip radius, R_{exp} , within the copper and copper alloys' structure (Fig.1) provided the results $R_{exp} = \hat{R} = 36$ cm, assuming that the R_{exp} – parameter is approximately equal to half the columnar grain diameter. It was also taken into account that the solidification rate is equal to rate of the isotherm liquidus velocity of movement. This condition is

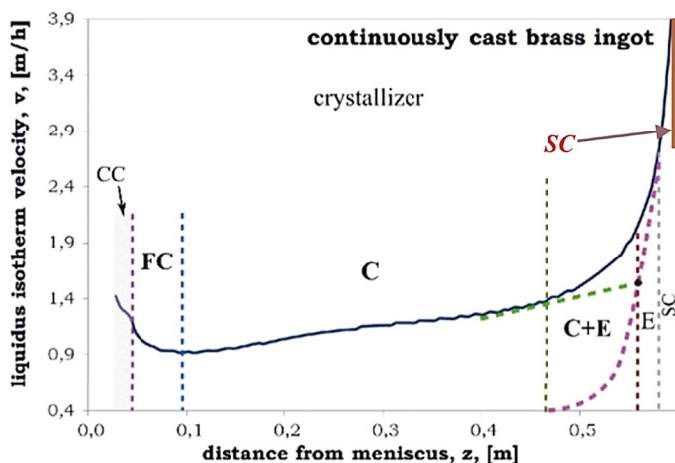


Fig. 2. Evolution of the liquidus isotherm velocity for the Cu-5Zn ingot's; pulling rate: $u = 90$ cm/min; crystallizer height: $H = 160$ cm

in agreement with the theory which shows that the s/l interface is in superposition with the liquidus isotherm and therefore both are moving with the same rate during solidification, [1]. Thus, it was taken that $v \equiv v_C \approx 2.0 \div 2.5$ cm/min, (for the columnar structure formation) with the v – velocity estimated on the basis of the numerical simulation of the temperature field within the solidifying brass ingot, Fig. 2.

It was also assumed that the diffusion coefficient in the liquid is equal to: $D = 3 \cdot 10^{-5} \div 7 \cdot 10^{-6}$ cm²/s, [2]. Eventually, the estimated values of the Peclet Number varies within the range: $Pe \approx 200 \div 1000$. It became evident that solidification of copper and copper alloys (formation of the columnar structure), usually, occurs at a high Peclet Number.

3. Growth Law for columnar structure formation

Since the Peclet Number presents its values higher than $Pe = 500$, therefore, the greater development in series of the Ivantsov's function, I_N ; $N = 0, 1, \dots, 5$, [9], is to be applied in the formulation of the Growth Law. It means that at least I_2 – development is to be used.

$$I_2 = 2Pe / (2Pe + 1) \quad (6a)$$

$$I_3 = (Pe^2 + 3Pe) / (Pe^2 + 4Pe + 2) \quad (6b)$$

$$I_4 = (3Pe^2 + 5Pe) / (3Pe^2 + 8Pe + 2) \quad (6c)$$

The development of the Growth Law uses the definition of the Ω – parameter, Fig. 3.

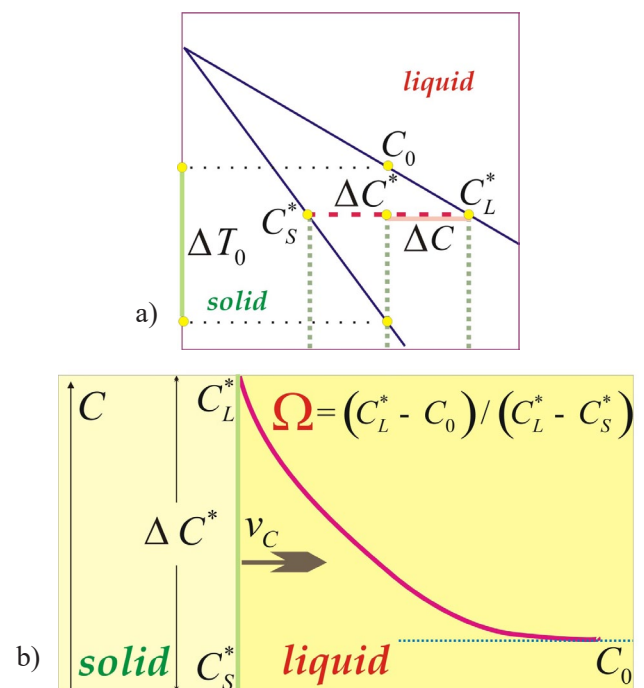


Fig. 3. Ω – solute supersaturation definition for the equilibrium solidification; a) localization of characteristic solute concentrations within an arbitrary phase diagram, b) solute concentration profile (red line) ahead of the s/l interface (green line), [10]

Solute concentration gradient, Eq. (2) can be defined on the basis of the scheme shown in Fig. 3a for equilibrium solidification:

$$G_C = -\frac{v_C}{D} \cdot \Delta C_0 \quad (7)$$

In this case, $\Delta C_0 = \Delta C^*$, when, $C_S^* \rightarrow C_0$, Fig. 3a. The equilibrium solidification is defined by the ΔT_0 – temperature range within which solidification process is completed.

The general definition of the ξ – index of the s/l interface stability is delivered by Eq. (8), [2]. This definition is valid when the Peclet Number satisfies the following inequality: $Pe \gg 1$, [2]. It should also be mentioned that $Pe \approx 200 \div 1000$ in the case of the copper and copper alloys' solidification as estimated above.

$$\xi = \pi^2 / (p \cdot Pe^2) \quad (8)$$

Introduction of the definition of the Peclet Number, Eq. (5) together with Eq. (7) into Eq. (8) yields:

$$\xi = 1 - \frac{2p}{\left\{1 + [4\pi \cdot D / (R \cdot v_C)]^2\right\}^{0.5} - 1 + 2p} \quad (9)$$

Combining Eq. (6a) and definition of the solute supersaturation (Fig. 3b) the following relationship is obtained:

$$C_L^* = \frac{C_0}{1 - (1-p) \cdot I_2} \quad (10)$$

Then, Eq. (2) combined with Eq. (10) yields:

$$\lambda_S = 2\pi \cdot \left[\frac{\gamma}{\Delta S \cdot \left\{ \frac{v_C}{D} \cdot \left[(p-1) \cdot \frac{C_0}{1 - (1-p) \cdot I_2} \right] \right\}} \right]^{0.5} \cdot \left[\frac{\gamma}{m_L \cdot \xi - G} \right] \quad (11)$$

In simplification, other developments of the Ivantsov's function can also be introduced into Eq. (2), with the assumption that $I_N = \Omega$ (strictly speaking, the I_2 – development can be replaced by the I_3 , or I_4 – development in series, respectively).

Then, after some rearrangements and application of the criterion of marginal stability, Eq. (1), three versions of the Growth Law are formulated:

a) for the I_2 – development,

$$\begin{aligned} \hat{R}^3 \cdot \left[\frac{\Delta S \cdot v_C}{m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C - G \cdot D \cdot p} \right] + \\ \hat{R}^2 \cdot \left[\frac{\Delta S \cdot D}{m_L \cdot \xi \cdot v_C \cdot (p-1) \cdot C_0 - G \cdot D} \right] - \\ \hat{R} \cdot \left[4\pi^2 \cdot \gamma \cdot D \cdot p \cdot v_C \right] - 4\pi^2 \cdot \gamma \cdot D^2 = 0 \end{aligned} \quad (12a)$$

b) for the I_3 – development,

$$\begin{aligned} \hat{R}^4 \cdot \left[\frac{\Delta S \cdot v_C^2 \cdot \left(m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C - G \cdot D \cdot p \right)}{C_0 \cdot v_C - G \cdot D \cdot p} \right] + \\ \hat{R}^3 \cdot \left[\frac{\Delta S \cdot D \cdot v_C \cdot \left(8m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C - G \cdot D \cdot (2+6p) \right)}{G \cdot D \cdot (2+6p)} \right] + \\ \hat{R}^2 \cdot \left[\frac{\Delta S \cdot D^2 \cdot \left(8m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C - 8G \cdot D \right)}{4\pi^2 \cdot \gamma \cdot D \cdot p \cdot v_C^2} \right] - \\ \hat{R} \cdot \left[4\pi^2 \cdot \gamma \cdot D^2 \cdot (2+6p) \cdot v_C \right] - \\ 32\pi^2 \cdot \gamma \cdot D^3 = 0 \end{aligned} \quad (12b)$$

c) for the I_4 – development,

$$\begin{aligned} \hat{R}^4 \cdot \left[\frac{3\Delta S \cdot v_C^2 \cdot \left(G \cdot D \cdot p - m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C \right)}{G \cdot D \cdot p - m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C} \right] + \\ \hat{R}^3 \cdot \left[\frac{2\Delta S \cdot D \cdot v_C \cdot \left(G \cdot D \cdot (3+5p) - 8m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C \right)}{G \cdot D \cdot (3+5p) - 8m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C} \right] + \\ \hat{R}^2 \cdot \left[\frac{8\Delta S \cdot D^2 \cdot \left(G \cdot D - m_L \cdot \xi \cdot (p-1) \cdot C_0 \cdot v_C \right)}{12\pi^2 \cdot \gamma \cdot D \cdot p \cdot v_C^2} \right] + \\ \hat{R} \cdot \left[8\pi^2 \cdot \gamma \cdot D^2 \cdot (3+5p) \cdot v_C \right] + \\ 32\pi^2 \cdot \gamma \cdot D^3 = 0 \end{aligned} \quad (12c)$$

where, $\hat{R} = R_{th.} \equiv R_{exp.}$

The formulated versions of the Growth Law, Eq. (12) contain the ξ – parameter. In particular, Eq. (12a) can be compared with the analogous version of the Growth Law delivered recently, in which $\xi = 1$, [10]. Contrary to mentioned version, Eq. (12a) does not present this controversial assumption, and an adequate definition of the ξ – index can be inserted into Eq. (12) in the current analysis.

4. Adaptation of the Growth Law to non-equilibrium solidification

The presented Growth Law, Eq. (12) can be related to non-equilibrium solidification. It is justified because limitations connected with equilibrium solidification (Fig. 3) do not need to be strictly respected. Moreover, the equilibrium solidification is virtual process, only. So, it is not possible to create conditions under which this process could be performed, especially in the industry of copper and copper alloys.

Therefore, the definition of the ξ – index is to be formulated/modified since its formulation given by Eq. (9) is too complicated to be applied to the Growth Law. Admittedly, nothing opposites

against introduction of the definition given by Eq. (9) into the formulated Growth Law, Eq. (12). However, in this case, the Growth Law cannot be solved analytically to predict the value of the $\hat{R} = R_{th.}$ – parameter, (value of the tip radius). It means that Eq. (12) could be solved numerically to find its roots, only.

Thus, the new simplification is proposed. First of all, the solidification path is assumed to be $C_L^* \in C_0 \Rightarrow C_E$ for non-equilibrium solidification instead of the $C_L^* \in C_0 \Rightarrow C_0/p$ – path, as valid for equilibrium solidification, Fig. 3a. The s/l interface path is assumed to be $C_S^* \in k \cdot C_0 \Rightarrow k \cdot C_E$ for non-equilibrium solidification instead of the $C_S^* \in k \cdot C_0 \Rightarrow C_0$ – path, as valid for equilibrium solidification, Fig. 3a.

It can be assumed (in approximation) that the following condition is satisfied in frame of the proposed simplification:

$$Pe \equiv \Omega = I_0 \quad (13)$$

According to Eq. (13) the tip of columnar grain cannot be paraboloidal as considered above but it becomes hemispherical in its shape, [8]. When it is assumed that the definition of the supersaturation can be applied for the completion of equilibrium solidification (for $C_S^* \rightarrow C_0$, Fig. 3a) then:

$$\Omega = 1 = Pe \quad (14)$$

Consequently, the definition of the ζ – index becomes as follows:

$$\zeta = \pi^2 / p \quad (15)$$

The above result, Eq. (15) is acceptable in comparison to that delivered by Eq. (3) and resultant simplification given by Eq. (4). This definition, Eq. (15) can be introduced into the formula of the Growth Law, Eq. (12) and under such condition. Now, Eq. (12) can be solved analytically. However, Eq. (15) is connected with equilibrium solidification, Fig. 3, which does not occur in some real processes. Thus, the definition of the ζ – index, Eq. (15) should be referred to non-equilibrium solidification which occurs in deviation from the equilibrium state as it appears in all real processes of crystal growth. Therefore, the scheme delivered for equilibrium solidification (Fig. 3a) will be subjected to a proper modification which is shown in Fig. 4.

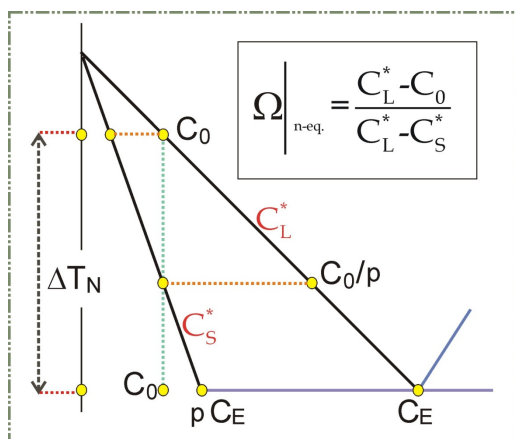


Fig. 4. Definition of the solute supersaturation within the ΔT_N – temperature range for non-equilibrium solidification

The scheme of non-equilibrium solidification (Fig. 4) contains the rule of equilibrium solidification as the particular case, when $\Delta T_N \rightarrow \Delta T_0$. The scheme is referred to real processes occurring with a given solidification rate $v_C \neq 0$, necessary for columnar structure formation.

The temperature range for non-equilibrium solidification is defined as:

$$\Delta T_N \equiv \Delta T_0 \Big|_{n=eq.} = T(C_0) - T_E \quad (16)$$

with

$$\Delta C_N \equiv \Delta C^* \Big|_{n=eq.} = C_E - (p \cdot C_E) \quad (17)$$

In the case, when $C_S^* \rightarrow p \cdot C_E$ the simplified definition for the solute supersaturation becomes equal to: $\Omega|_{n=eq.} = (C_E - C_0) / [(1 - p) \cdot C_E]$, Fig. 4. Taking into account that $Pe = \Omega|_{n=eq.}$, the new definition of the ζ – index becomes equal to:

$$\zeta = \pi^2 / (p \cdot \Omega_{n=eq.}^2) = (\pi^2 / p) \cdot [(1 - p) \cdot C_E / (C_E - C_0)]^2 \quad (18)$$

The above definition, Eq. (18) is to be inserted into the polynomials named as the Growth Law, Eq. (12). It allows to solve these equations analytically.

5. Concluding remarks

Three versions of the Growth Law for the columnar structure have been formulated, see Eq. (12). Since the Peclet Number varies within the range $Pe \approx 200 \div 1000$ as estimated, therefore, it is postulated to apply the first version of the Growth Law, Eq. (12a) when the Peclet Number is within the range $200 \leq Pe \leq 500$. This condition is in an agreement with that well known in the theory of solidification, [2].

Consequently, the second version of the Growth Law, see Eq. (12b) can satisfy the range of the Peclet Number: $500 \leq Pe \leq 750$, and the third version of the Growth Law, Eq. (12c) should be attributed to the range: $750 \leq Pe \leq 1000$.

All the three versions of the Growth Law can be solved analytically due to the new definition of the ζ – index of stability.

The new definition of the ζ – index is given by Eq. (18), and is connected with the real processes of solidification occurring in deviation from equilibrium.

The suggested definition of the ζ – index allows to eliminate/avoid the unacceptable condition delivered by Eq. (3) resulting in the simplification according to which solidus line would be in the superposition with the line of zero's solute solubility in the solid. Moreover, the mentioned superposition imposes the condition $p = 0$, Eq. (4) which has not physical/thermodynamic meaning.

The new definition of the ζ – index can be easily calculated with the use of some parameters available from the phase diagram, in particular, from the Cu-X phase diagram, where X – denotes the alloying elements in the copper alloys. But first

of all, the p – partition ratio conserves its real value connected with a given phase diagram, Cu-X.

The proposed Growth Law has the physical meaning since it indicates that at the imposed pulling rate of copper or copper alloys' ingot through the crystallizer, when the columnar grains formation is supposed to a constant growth rate v_C , and to a positive constant thermal gradient resulting from the heat transfer (ingot \rightarrow crystallizer), and when the X – solute concentration is well known, one and only one value of the \hat{R} – tip radius can be expected within the ingot's morphology.

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REFERENCES

- [1] W. Wołczyński, A. Ivanova, P. Kwapisiński, *Procedia Manufacturing* **30**, 459-466 (2019). www.elsevier.com/locate/procedia
- [2] W. Kurz, D.J. Fisher, *Fundamentals of Solidification*, Ed. Trans. Tech. Publications, 1998.
- [3] J. Szajnar, *Journal of Materials Processing Technology* **157-158**, 761-764 (2004).
- [4] P. Kwapisiński, A. Ivanova, B. Kania, W. Wołczyński, *Archives of Foundry Engineering* **17** (1), 109-114 (2017).
- [5] R. Trivedi, *Journal of Crystal Growth*, **49**, 219-232 (1980).
- [6] I. Jin, G.R. Purdy, *Journal of Crystal Growth* **23**, 29-36 (1974).
- [7] J.S. Langer, H. Müller-Krumbhaar, *Journal of Crystal Growth* **42**, 11-14 (1977).
- [8] W. Kurz, D.J. Fisher, *Acta Metallurgica* **29**, 11-20 (1981).
- [9] G.P. Ivantsov, *Doklady Akademii Nauk SSSR* **58**, 567-572 (1947).
- [10] P. Kwapisiński, Z. Lipnicki, A. Ivanova, W. Wołczyński, *Archives of Foundry Engineering* **17** (2), 49-54 (2017).
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