

RESEARCH PAPER

MATHEMATICAL EQUATION FOR IMPURITY DISTRIBUTION AFTER SECOND PASS OF ZONE REFINING

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ABSTRACT

A mathematical equation has been derived that describes impurity distribution in ingot after second pass of zone refining. While an exponential impurity distribution is calculated by a simplified model after first pass, second pass is described by mixed linear - exponential model. Relationship of transformed impurity concentration is constant over whole length of semi-infinite ingot for first pass. However, it has linear trend for second pass. Last part of molten zone at infinity solidifies differently and can be described mathematically as directional crystallization. A mathematical tool devised for second pass of zone refining can be tried to be used for derivation of functions of more complex models that would describe impurity distribution in more realistic way compared to simplified approach. Such models could include non-constant distribution coefficient and/or shrinking or widening molten zone over a length of ingot.

Keywords: zone refining; second pass; mathematical description of impurity distribution

INTRODUCTION

A distribution of impurities between liquid and solid phase during crystallization was recognized many years ago. These phenomena were already mentioned by Nerst in his paper about theory of the kinetics of heterogeneous reactions in 1904 [1].

A zone refining (zone melting) technique is known almost one century. It is based on a different concentration of impurity in solid and liquid at their phase boundary. According to Feigelson first reported use of zone melting was by Kapica in 1928 [2 and citation thereof].

Among other scientists W. G. Pfann worked intensively on theory and practice of zone melting and other improved techniques of this kind. He describes them in his book [3]. When ingot with evenly distributed impurity over its whole volume is treated by zone refining, an impurity accumulates - when distribution coefficient is less than one - in melt. Mathematical equation describing distribution of impurity after first pass can be written in a form

$$c_{s1}(x) = c_0 + c_0 \cdot (k - 1) \cdot e^{-\frac{k \cdot x}{h}} \quad (1.)$$

where “ $c_{s1}(x)$ ” is concentration of impurity in solid phase after first pass, “ c_0 ” is initial concentration of evenly distributed impurity, “ k ” is distribution coefficient (ratio of impurity concentration in solid and liquid phase), “ h ” is width of molten zone and “ x ” is distance from beginning of ingot. Equation (1) holds when width of molten zone is constant during zone melting, cross-section area is constant, “ k ” keeps constant, no volume changes take place during solidification, mixing of melt is perfect and no diffusion takes place in solid phase. An above equation is valid for full ingot length except for last molten zone

which solidifies fractionally [3]. Equation (1) is sometime ascribed to Pfann, however he gives credit for derivation of this equation to W. T. Read [4].

In a chapter about multi-pass zone melting in [3] Pfann mentions “*It would be most helpful to have a general equation that expresses solute concentration as a function of distance, for any number of passes through an ingot of specified length. No such equation has been derived. While the concepts of zone refining are simple, it is apparently difficult to describe multi-pass operations mathematically.*” Therefore several mathematical methods were devised to cope with this problem, e.g. [5-10]. They are, in principle, iterative numerical methods.

Situation with mathematical solution of zone melting has changed when powerful computer become readily available. Specific simulation software can be written and run where dynamic changes during zone melting can be analyzed [11-13 and citations thereof]. Although simulations are helpful, data need to be fed into software which is specific to the analyzed parameters.

METHODS

Mathematical description of impurity distribution during second pass of zone refining

The details of method for evaluation of mathematical equations describing impurity distribution after second pass of zone refining is shown in Appendix.

Integral material balance equation of zone refining for second and higher passes was “resistant to solution” for almost 70 years. Finally, application of multidisciplinary approach and transformation of integral equation into its differential form proved fruitful leading to an analytical solution.

RESULTS AND DISCUSSION

Resulting equation of impurity distribution after second pass of zone refining is as follows:

$$c_{s2}(x) = c_0 + c_0 \cdot (k - 1) \cdot (2 - e^{-k}) \cdot e^{-\frac{k \cdot x}{h}} + \frac{k}{h} \cdot c_0 \cdot (k - 1) \cdot e^{-k} \cdot x \cdot e^{-\frac{k \cdot x}{h}} \quad (2)$$

It can be written in more convenient way as:

$$c_{s2}(x) = c_0 \cdot \left[1 + (a_{2,0} + a_{2,1} \cdot x) \cdot e^{-\frac{k \cdot x}{h}} \right] \quad (2a.)$$

where

$$\begin{aligned} a_{2,0} &= a_{1,0} \cdot (2 - e^{-k}); \\ a_{2,1} &= a_{1,0} \cdot \frac{k}{h} \cdot e^{-k}; \\ a_{1,0} &= k - 1 \end{aligned} \quad (2b.)$$

Boundary concentration, i.e. concentration of impurity at position $x=0$ is $k \cdot c_0$ for first pass. It is intuitively expected that boundary concentration should, at position $x=0$, equal $k^2 \cdot c_0$ for a second pass. However, as follows from equation (2) boundary concentration is different. Reason for it is as follows: impurity is evenly distributed over whole volume of ingot before first pass. Concentration of impurity in first molten zone with width of "h" is constant and equals c_0 . Therefore ingot at position $x=0$ solidified with impurity concentration $k \cdot c_0$. This is not valid for second pass since distribution of impurity over a volume of ingot is not constant anymore. It needs to be calculated as average concentration within molten zone as follows

$$c_{L2}(0 \div h) = \frac{1}{h} \cdot \int_0^h (c_0 + c_0 \cdot (k - 1) \cdot e^{-\frac{k \cdot t}{h}}) \cdot dt = \frac{1}{h} \cdot (c_0 \cdot h - c_0 \cdot \frac{h}{k} \cdot (k - 1) \cdot e^{-k} + c_0 \cdot \frac{h}{k} \cdot (k - 1)) \quad (3)$$

Ingot at boundary position $x=0$ solidifies as

$$c_{s2}(0) = k \cdot c_{L2}(0 \div h) = \frac{k}{h} \cdot (c_0 \cdot h - c_0 \cdot \frac{h}{k} \cdot (k - 1) \cdot e^{-k} + c_0 \cdot \frac{h}{k} \cdot (k - 1)) = c_0 + c_0 \cdot (k - 1) \cdot (2 - e^{-k}) \quad (4)$$

Visualization of impurity distribution after second pass of zone refining

Surface of impurity concentration as a function of ingot length and distribution coefficient with dimensionless molten zone width of 0.2 is shown in Fig. 1. All units are arbitrary. Isolines of distribution coefficient run from left to right.

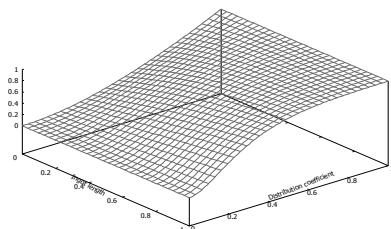


Fig. 1 Surface of impurity concentration as a function of ingot length and distribution coefficient [19]

Surface of impurity concentration as a function of ingot length and molten zone width with distribution coefficient of 0.2 is shown in Fig. 2. All units are arbitrary. It is seen in Fig. 2 that efficiency of impurity removal increases non-linearly with increasing molten zone width.

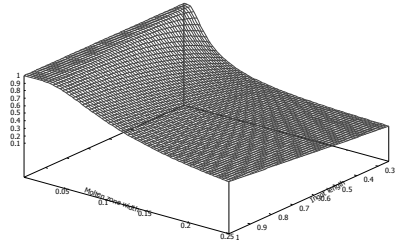


Fig. 2 Surface of impurity concentration as a function of ingot length and molten zone width [19]

Linearization of impurity distribution equations for first and second pass of zone refining

It is worth to note an interesting property of equation (1) and (2). When constant c_0 is subtracted from both sides, then both sides are divided by exponential member and initial impurity concentration the following relations hold:

$$\frac{c_{s1}(x) - c_0}{c_0 \cdot e^{-\frac{k \cdot x}{h}}} = (k - 1) \quad (5)$$

$$\frac{c_{s2}(x) - c_0}{c_0 \cdot e^{-\frac{k \cdot x}{h}}} = (k - 1) \cdot (2 - e^{-k}) + \frac{k}{h} \cdot (k - 1) \cdot e^{-k} \cdot x \quad (6)$$

Left side of equation (5) is constant for all values of independent variable (length of ingot) while in case of equation (6) it keeps linear trend. Note, that both sides of equation (5) and (6) are dimensionless.

CONCLUSION

A mathematical description of impurity distribution in ingot after second pass of zone refining has been derived using integral-differential approach. It is of mixed linear - exponential type. From a mathematical point of view an integral - differential approach seems worth to try in search of equations for more complex models of zone refining such as non-constant distribution coefficient and/or shrinking or widening of molten zone over length of ingot.

Efficiency of impurity removal depends non-linearly on both distribution coefficient as well as molten zone width.

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One of the authors (M.S.) would like to dedicate this paper to his teacher, colleague and friend, now retired Associate Professor Jozef Ďurišin, PhD.

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19. Gnuplot release 5.4.0, July 2020 (www.gnuplot.info)

Appendix

Evaluation of equation for second pass of zone melting

Distribution of impurity in zone refined ingot after first pass is mathematically described by eq. (1). Distribution of impurity during second pass is schematically shown in Fig. 3. This approach is based on material balance before and after second pass. A problem with end part of ingot can be solved mathematically as zone refining of semi-infinite sample. From a practical point of view, last ingot zone with width of “h” can be treated as fractional solidification. It accumulates high concentration of impurity.

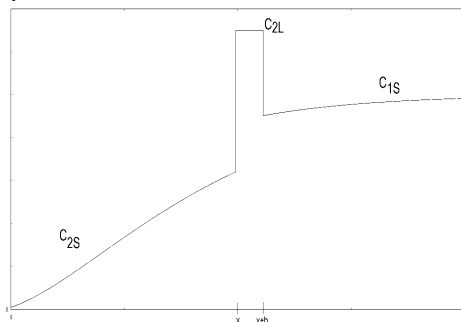


Fig. 3 Schematic distribution of impurity during second pass of zone refining

Material balance equation of impurity distribution for second pass that follows after first pass of zone refining can be written as follows

$$\int_0^x c_{s2}(t) \cdot dt + \frac{h}{k} \cdot c_{s2}(x) = \int_0^{x+h} \left(c_0 + c_0 \cdot (k-1) \cdot e^{-\frac{kt}{h}} \right) dt \tag{7.}$$

Right side of equation (7) can be evaluated as it is known function describing impurity distribution in ingot after first pass. Then a substitution $y = \int_0^x c_{s2}(t) \cdot dt$ is applied. Second member of equation (7) on left side is thus $y' = \frac{dy}{dx}$ multiplied by $\frac{h}{k}$. Equation (7) can be written in a form

$$y + \frac{h}{k} \cdot y' = g(x) \tag{8.}$$

where

$$g(x) = \int_0^{x+h} \left(c_0 + c_0 \cdot (k-1) \cdot e^{-\frac{kt}{h}} \right) dt$$

Multiplying both sides of equation (7) by $\frac{k}{h}$ gives non-homogeneous linear differential equation of first order [15] in a form

$$\frac{k}{h} \cdot y + y' = \frac{k}{h} \cdot \left(L + c_0 \cdot x - M \cdot e^{-\frac{kx}{h}} \right) \tag{9.}$$

where

$$L = c_0 \cdot h + \frac{h}{k} \cdot c_0 \cdot (k-1)$$

$$M = \frac{h}{k} \cdot c_0 \cdot (k-1) \cdot e^{-k}$$

This kind of differential equations is used to solve integral-differential problems, e.g. [16-18] – integral equation (7) is transformed into differential form (9).

General solution of equation (9) is [15]:

$$y = \frac{1}{E(x)} \cdot \left(\int E(x) \cdot g(x) \cdot dx + C \right) \tag{10.}$$

where $E(x) = e^{\int f(x) \cdot dx} = e^{\frac{kx}{h}}$

Integrating function $g(x)$ in equation (8) and inserting result into equation (9) gives a solution

$$y = \left(L + c_0 \cdot x - \frac{h}{k} \cdot c_0 \cdot \frac{k}{h} \cdot M \cdot x \cdot e^{-\frac{kx}{h}} + C \cdot e^{-\frac{kx}{h}} \right) \tag{11.}$$

Constants L and M are shown in equation (9), constant C need to be evaluated from boundary condition – equation (4). As follows from equations (7), (8) and (11), a final form of mathematical description of impurity distribution after second pass of zone refining can be written as

$$c_{s2}(x) = \frac{dy}{dx} = c_0 + c_0 \cdot (k-1) \cdot (2 - e^{-k}) \cdot e^{-\frac{kx}{h}} + \frac{k}{h} \cdot c_0 \cdot (k-1) \cdot e^{-k} \cdot x \cdot e^{-\frac{kx}{h}} \tag{12.}$$

Verification of equation for second pass of zone refining

Check of correctness of derived equation (2) for second pass of zone refining is done by inserting of equation (1) and (2) into material balance equation (7):

$$\int_0^{x+h} \left(c_0 + c_0 \cdot (k-1) \cdot e^{-\frac{kt}{h}} \right) \cdot dt = c_0 \cdot (x+h) - \frac{h}{k} \cdot c_0 \cdot (k-1) \cdot e^{-k} \cdot e^{-\frac{kx}{h}} + \frac{h}{k} \cdot c_0 \cdot (k-1) \tag{13a.}$$

$$\frac{h}{k} \cdot c_{s2}(x) = \frac{h}{k} \cdot c_0 + \frac{h}{k} \cdot P \cdot e^{-\frac{kx}{h}} + \frac{h}{k} \cdot Q \cdot x \cdot e^{-\frac{kx}{h}} \tag{13b.}$$

where

$$P = c_0 \cdot (k - 1) \cdot (2 - e^{-k})$$

$$Q = \frac{k}{h} \cdot c_0 \cdot (k - 1) \cdot e^{-k}$$

$$\int_0^x c_{s2}(t) \cdot dt = c_0 \cdot x - \left(\frac{h}{k} \cdot P + Q \cdot \frac{h^2}{k^2} \right) \cdot e^{-\frac{k \cdot x}{h}} - Q \cdot \frac{h}{k} \cdot x \cdot e^{-\frac{k \cdot x}{h}} + \frac{h}{k} \cdot P + Q \cdot \frac{h^2}{k^2} \quad (13c.)$$

$$\begin{aligned} & \frac{h}{k} \cdot P + Q \cdot \frac{h^2}{k^2} + \frac{h}{k} \cdot c_0 + c_0 \cdot x - Q \cdot \frac{h^2}{k^2} \cdot e^{-\frac{k \cdot x}{h}} + \frac{h}{k} \cdot P \cdot e^{-\frac{k \cdot x}{h}} - \\ & \frac{h}{k} \cdot P \cdot e^{-\frac{k \cdot x}{h}} + \frac{h}{k} \cdot Q \cdot x \cdot e^{-\frac{k \cdot x}{h}} - \frac{h}{k} \cdot Q \cdot x \cdot e^{-\frac{k \cdot x}{h}} = c_0 \cdot (x + h) - \\ & \frac{h}{k} \cdot c_0 \cdot (k - 1) \cdot e^{-k} e^{-\frac{k \cdot x}{h}} + \frac{h}{k} \cdot c_0 \cdot (k - 1) \quad (14.) \end{aligned}$$

Last four members on left side of equation (14) cancel each other and remaining members on left and right side are equal – material balance equation (7) is satisfied.