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Mathematical modelling of macrosegregation in binary alloys induced by convection

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RESUMO

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A macrosegregação em lingotes de ligas metálicas pode influenciar de maneira significativa a qualidade da produção. Tal defeito se caracteriza pela severa variação química do material em escala macroscópica, enquanto lingotes de grandes dimensões podem ainda ser afetados por cavidade de encolhimento desenvolvida ao longo da porção central. Prever suas ocorrências por meio de simulações computacionais é uma tarefa que deve ser aperfeiçoada. Esta tese apresenta: um modelo matemático 2D para a formação da cavidade central utilizando balanço de massa e conservação de energia com calor latente no termo fonte, capaz de verificar numericamente a eficácia de aparatos atualmente usados pela indústria para reduzir a profundidade da cavidade; um modelo de macrosegregação 2D com formulação de domínio único incluindo momento, calor, massa e conservação de soluto, o qual reproduz dados presentes na literatura; e por último, um novo modelo de macrosegregação 1D sujeito à contração, consistindo em três regiões distintas limitadas por três interfaces móveis, para o qual uma solução por similaridade válida para tempos pequenos foi obtida e validada por dados numéricos disponíveis na literatura, servindo como condição inicial para o problema não-similar usado para traçar diretrizes que podem, em certas circunstâncias, reduzir o desvio padrão sobre a concentração inicial de soluto em até 40%.

Palavras-chave: macrosegregação, similaridade, solidificação.

ABSTRACT

ASSUNÇÃO, M. **Mathematical modelling of macrosegregation in binary alloys induced by convection**. 2021. 149 p. Tese (Doutorado em Ciências – Ciências de Computação e Matemática Computacional) – Instituto de Ciências Matemáticas e de Computação, Universidade de São Paulo, São Carlos – SP, 2021.

The occurrence of macrosegregation in ingot casting can actuate to depletion of the product's final quality. Such defect can be described as a severe variation on macroscopic scale of chemical species that compose the alloy, whilst large ingots can also be severely affected by shrinkage cavity along the center line. The prediction of its occurrence via computational simulations has yet to be improved. This thesis provides: a 2D mathematical model for the formation of the shrinkage cavity using mass balance, and energy conservation with latent heat as source term, able to numerically verify the efficiency of apparatus currently used in the industry to reduce the cavity depth; a 2D macrosegregation model with a single-domain formulation including momentum, heat, mass and solute conservation, that reproduces results available in the literature; lastly, a novel 1D macrosegregation model undergoing shrinkage is presented, consisting of three distinct regions bounded by three moving interfaces, for which a similarity solution valid for small times was obtained and validated against numerical data, serving as initial condition to the non-similar problem used to draw some guidelines that can, in some circumstances, reduce the standard deviation on the initial solute concentration by up to 40%.

Keywords: macrosegregation, similarity solution, solidification.

LIST OF FIGURES

Figure 1.1 – Casting steps for metal alloys. Adapted from (OVAKO..., 2014b). The dashed red line shows the domain of the problem addressed.	22
Figure 1.2 – Cell interface in transparent alloy (CBr ₄ - <i>tetrabromomethane</i>). Adapted from (FLEMINGS, 1974)	24
Figure 1.3 – Fully developed cells in metallic binary alloy Al-Cu (aluminum and copper). Adapted from (FLEMINGS, 1974)	25
Figure 1.4 – Transversal slice on cellular structure in metallic binary alloy Pb-Sb (lead and antimony). Adapted from (FLEMINGS, 1974)	26
Figure 1.5 – Changes in the shape of the solidification structures by increasing their growth speed: (a) regular cell growing at low speed; (b) regular cell growing in the <100> direction; (c) flanged cell; (d) dendrite showing periodic lateral branches. Adapted from (FLEMINGS, 1974)	26
Figure 1.6 – Intersection coordinates between the plane and the coordinate system. Adapted from (FREDRIKSSON; ÅKERLIND, 2008).	27
Figure 1.7 – Diagram for dendrite growth during solidification of an alloy. Adapted from (FLEMINGS, 1974)	27
Figure 1.8 – Detachment of the secondary dendritic arm portion in relation to the original primary arm. Adapted from (FLEMINGS, 1974)	28
Figure 1.9 – Convective flux on liquid and mushy zones during solidification process. . .	28
Figure 1.10–Example of numerical solution considering Sn-10 % Pb alloy. The velocity field is computed on a two-dimensional domain and unidirectional solidification(a). It is also possible to see different lead concentrations across the solidified material (b). Adapted from (FREDRIKSSON; ÅKERLIND, 2006).	29
Figure 1.11–Differences in solute concentration (C) between the center and the side of the piece. Adapted from (FREDRIKSSON; ÅKERLIND, 2006).	29
Figure 1.12–On the left and in the details are areas of occurrence of different forms of macrosegregation. On the right are represented the structures taken into account in the construction of models of multiple domains. Adapted from (PICKERING, 2013) and (FREDRIKSSON; ÅKERLIND, 2006).	30
Figure 1.13–Photographed cross-sections of stearin ingot showing the pipe formation. Adapted from (BREARLEY; BREARLEY, 1918).	31
Figure 1.14–Comparison between the dimensions of ingots, macrosegregation defects and interdendritic spacing. Adapted from (COLPAERT; SILVA, 2008).	32

Figure 1.15–Phase diagram of binary eutectic system	33
Figure 1.16–Phase diagram of binary non-eutectic system	33
Figure 2.1 – Ingot and hot-top geometry. Extracted from (BROLUND <i>et al.</i> , 1986).	41
Figure 2.2 – Volume balance displaying the liquid surface and the position of the solidification front at times t and $t + dt$. Adapted from (RAIHLE; FREDRIKSSON, 1994).	42
Figure 2.3 – Permeability vs liquid fraction, squares represent experimental data and the solid line represents the results obtained from permeability equation. Adapted from (WEST, 1985)	46
Figure 2.4 – Single-phase Stefan problem. (a) domain configuration, (b) position of liquid-solid interface. Adapted from (CRANK, 1987).	56
Figure 2.5 – Space-time diagram for the two-phases Stefan problem	58
Figure 2.6 – Notations of domains and mappings for the ALE description of motion.	62
Figure 3.1 – Solidification and formation of central cavity.	65
Figure 3.2 – Shrinkage cavity sketch under Dirichlet boundary condition.	66
Figure 3.3 – Pipe formation scheme under Neumann boundary conditions.	67
Figure 3.4 – Geometry of steel ingot. Measures in mm.	69
Figure 3.5 – Mould sketch based on original mould dimensions.	70
Figure 3.6 – Contraction cavities for 4.2 ton ingot. To the right without using the hot-top and to the left with 20cm hot-top from the top, along the mould wall.	71
Figure 3.7 – Shrinkage cavity profiles for different values of heat transfer coefficient, $D = 33$ cm.	72
Figure 3.8 – Shrinkage cavity profiles for different values hot-top length, $h = 120$ W/m ⁻² K ⁻¹	72
Figure 3.9 – (a) Maximum temperature obtained in the computational domain for ingots of 4.2 ton over time, and (b) Oscillation on the temperature curve for different mesh sizes.	73
Figure 3.10–Temperature curve over time for 4.2 ton ingot in two mesh sizes.	73
Figure 4.1 – Phase diagram for Fe-C alloy.	75
Figure 4.2 – Mould geometry for single-domain formulation.	76
Figure 4.3 – Staggered grid showing computational domain and different cells for each variable.	79
Figure 4.4 – Discretization of u -velocity near the wall. North boundary on the top, West boundary on the bottom.	79
Figure 4.5 – Liquid fraction after 200s. As presented in (ASSUNÇÃO; VYNNYCKY, 2018).	81
Figure 4.6 – Mixture concentration after 6000s. As presented in (ASSUNÇÃO; VYNNYCKY, 2018).	81

Figure 4.7 – Velocity field and streamlines for the domain half occupied by mush, half occupied by liquid phase, at an early stage of solidification process. As presented in (ASSUNÇÃO; VYNNYCKY, 2018).	81
Figure 4.8 – Mixture solute concentration comparison for different mesh sizes.	82
Figure 4.9 – Mixture solute concentration comparison for different values of ε	83
Figure 5.1 – Solidification with shrinkage: (a) initial configuration at $t = 0$; (b) after time $t > 0$	86
Figure 5.2 – Al-rich side of the linearized phase diagram for the Al-Cu system. L denotes liquid phase, and α and θ denote two solid phases.	87
Figure 5.3 – Schematic of the solution structure for small τ in the η -space. The dashed line indicates a boundary layer in θ of width $\tau^{1/2}$, with $\eta - 2 \sim \tau^{1/2}$	102
Figure 5.4 – The curve in (β, C_0) -space which determines whether $\chi_s = 0$ or $\chi_s > 0$ ($R = 1$)	105
Figure 5.5 – χ_s as a function of β for three values of C_0 ($R = 1$)	106
Figure 5.6 – The curve in (β, C_0) -space for different values of R	107
Figure 5.7 – The curve in (β, C_0) -space for $R = 1.3$ and different values of superheat δT	107
Figure 5.8 – The curve in (β, C_0) -space for $R = 1.3$ and different cooling surface temperatures T_w	108
Figure 5.9 – θ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	108
Figure 5.10– χ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	109
Figure 5.11– χ as a function of η for three values of δT and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$	109
Figure 5.12– χ as a function of η for three values of cooling boundary temperature T_w and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$	109
Figure 5.13– $\tilde{U}$ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	110
Figure 5.14– $\tilde{U}$ as a function of η for three values of superheat δT and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$	110
Figure 5.15– $\tilde{U}$ as a function of η for three values of cooling boundary temperature T_w and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$	111
Figure 5.16– η_{sol} (a) and η_{liq} (b) as functions of β for four values of R . As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	112
Figure 5.17– η_{sol} (a) and η_{liq} (b) as functions of β with $R = 1.3$ for different values of superheat δT	112
Figure 5.18– η_{sol} (a) and η_{liq} (b) as functions of β with $R = 1.3$ for different temperatures of cooling boundary T_w	112
Figure 5.19–The solute concentration in the solid, C_{solid} , as a function of β for four values of R . As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	113

Figure 5.20– $\theta(\tau_1)$ as a function of Y inside the solid region for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$	114
Figure 5.21– $\theta(\tau_1)$ as a function of Y inside the mush region for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$	115
Figure 5.22– $\chi(\tau_1)$ as a function of Y for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$	115
Figure 5.23– $\hat{U}(\tau_1)$ as a function of Y for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$	115
Figure 5.24–Positions of solid-mush, mush-liquid, and liquid interfaces with $\beta = 0$ for different density ratios: (a) $R = 1.0$; (b) $R = 1.1$; (c) $R = 1.2$; (d) $R = 1.3$	117
Figure 5.25–Positions of solid-mush, mush-liquid, and liquid interfaces with $\beta = 1$ for different density ratios: (a) $R = 1.0$; (b) $R = 1.1$; (c) $R = 1.2$; (d) $R = 1.3$	118
Figure 5.26–Final solute concentration across solidified domain with $\beta = 0$	119
Figure 5.27–Final solute concentration across solidified domain with $\beta = 1$	119
Figure 5.28–Final solute concentration across solidified domain for different values of superheat δT . Considering $\beta = 0$ and $R = 1.3$	120
Figure 5.29–Final solute concentration across solidified domain for different values of cooling surface temperature T_w . Considering $\beta = 0$ and $R = 1.3$	121
Figure 5.30–Final solute concentration across solidified domain for different values of superheat δT and cooling surface temperature T_w . Considering $\beta = 0$ and $R = 1.3$	122
Figure 5.31–Comparison between solid-mush and mush-liquid interfaces vs small-time assumptions.	123
Figure 5.32–Position of the solid-mush interface Y_s vs τ for different values of τ_0 . Considering $\beta = 1$ and $R = 1.0$	123
Figure 5.33–Position of the mush-liquid interface Y_l vs τ for different values of τ_0 . Considering $\beta = 1$ and $R = 1.0$	124
Figure 5.34–Comparison for the mixture concentration with the results in (VOLLER, 1997) for: (a) $\beta = 0$; (b) $\beta = 1$. Adapted from (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).	126
Figure 5.35–Summation of final solute concentration for: (a) $\beta = 0$; (b) $\beta = 1$	127
Figure 5.36–Final solute concentration across solidified domain for different mesh sizes. Considering $\beta = 0$ and $R = 1.3$	128
Figure 5.37–Final solute concentration across solidified domain for tolerances. Considering $\beta = 0$ and $R = 1.3$	128

LIST OF TABLES

Table 1 – Tectic type reactions. Adapted from (FREDRIKSSON; ÅKERLIND, 2012) .	34
Table 2 – Physical properties used for pipe-formation numerical simulation.	70
Table 3 – Solidification time for 4.2 ton steel ingots with shrinkage cavity. (*) Data from (RAIHLE; FREDRIKSSON, 1993).	71
Table 4 – Solidification time, computing time, and memory requirements for different mesh sizes.	73
Table 5 – Physical parameters adopted on single-domain model.	80
Table 6 – Mesh sizes with uniform element size h , number of elements and the time it took to obtain the results compared in Fig. 4.8.	82
Table 7 – Accuracy and decrease in computing times for increasing values of ε . Considering $h = 5e-3$	84
Table 8 – Parameters for computations for Al-5 wt% Cu	87
Table 9 – Mathematical models valid for three or two-regions formulations, defined by Governing Equations (G.E.), Boundary and Interfacial Conditions (B.C.), and Initial Values (I.V.).	114
Table 10 – Initial domain configuration for $\tau > 0$	116
Table 11 – Considering $\beta = 0$, τ_l and τ_m are respectively the time it takes for the liquid and mush regions to vanish, while $Y_l^{final}=Y_\infty(\tau_l)$ and $Y_m^{final}=Y_s(\tau_m)$	118
Table 12 – Considering $\beta = 1$, τ_l and τ_m are respectively the time it takes for the liquid and mush regions to vanish, while $Y_l^{final}=Y_\infty(\tau_l)$ and $Y_m^{final}=Y_s(\tau_m)$	120
Table 13 – Standard deviation (α) calculated for each combination of parameters.	120
Table 14 – Non-dimensional times τ_l , τ_m necessary for the disappearance of liquid and mush regions, respectively; standard deviation (α) on c_0 calculated for different values of superheat δT and cooling boundary temperature T_w . Considering $\beta = 0$ and $R = 1.3$	122
Table 15 – Absolute error on initial solid-mush and mush-liquid interfaces, with the reference values $Y_s^* = Y_s(\tau_0 = 1e-4)$ and $Y_l^* = Y_l(\tau_0 = 1e-4)$. Considering $\beta = 1$ and $R = 1.0$	124
Table 16 – Categorization of solidification process into eutectic, non-eutectic, or changing from latter to former at the time τ_{eut} , and the position $Y_{eut} = Y_s(\tau_{eut})$	125
Table 17 – Percentage (%) of final domain that solidified under eutectic conditions.	125

LIST OF SYMBOLS

ρ_0 — Initial density [kg/m³]

$\mathbf{u}$ — Velocity vector [m/s]

μ — Dynamic viscosity [Ns/m²]

p — Pressure [N/m²]

χ — Liquid fraction [1]

$H(\chi)$ — Permeability

c_p — Specific heat [J/(kg K)]

c_{pl} — Specific heat in the liquid phase [J/(kg K)]

c_{ps} — Specific heat in the solid phase [J/(kg K)]

k — Thermal conductivity [W/(m K)]

k_l — Thermal conductivity in the liquid phase [W/(m K)]

k_s — Thermal conductivity in the solid phase [W/(m K)]

ΔH_f — Latent heat [J/kg]

T — Temperature [K]

c_l — Solute concentration in the liquid phase [w.t.%]

c_s — Solute concentration in the solid phase [w.t.%]

k_p — Partition coefficient

c_m — Mixture concentration in the single-domain model [w.t.%]

D — Diffusion coefficient [m²/s]

ε — Numerical parameter in the single-domain model [1]

Q — Constant heat removal in the single-domain model [W/m²]

T_w — Wall temperature [K]

T_{eut} — Eutectic temperature [K]

C_0 — Initial solute concentration [w.t.%]

y_s — Position of the solid-mush interface [m]

y_1 — Position of the mush-liquid interface [m]

y_∞ — Position of the liquid interface [m]

Pr — Prandtl number [1]

Ra — Rayleigh number [1]

Ga — Galilei number [1]

Da — Darcy number [1]

St — Stefan number [1]

Le — Lewis number [1]

CONTENTS

1	INTRODUCTION	21
1.1	Ingot solidification	23
1.1.1	<i>Phase Diagrams</i>	32
1.1.2	<i>The Mullins-Sekerka Instability</i>	35
1.2	Contributions	35
1.3	Outline	36
2	LITERATURE REVIEW	39
2.1	Pipe formation modelling	40
2.1.1	<i>Fredriksson and co-workers</i>	40
2.1.2	<i>Radovic et al (RADOVIC et al., 2010)</i>	43
2.2	Single domain modelling	44
2.2.1	<i>Momentum conservation</i>	44
2.2.2	<i>Heat conservation</i>	46
2.2.3	<i>Mass and solute conservation</i>	47
2.2.4	<i>Boundary conditions</i>	49
2.3	Multi-domains modelling	52
2.3.1	<i>Flemings and co-workers</i>	52
2.3.2	<i>Szekely and Jassal (SZEKELY; JASSAL, 1978)</i>	53
2.3.3	<i>Voller (VOLLER, 1997)</i>	53
2.4	Stefan problem	56
2.5	Similarity solutions	58
2.6	Arbitrary Lagrangian-Eulerian method	61
3	PIPE FORMATION MODELLING	65
3.1	Mathematical formulation	66
3.2	Numerical Implementation	69
3.3	Numerical Results	69
4	SINGLE DOMAIN MODELLING	75
4.1	Mathematical Formulation	76
4.2	Nondimensionalization	77
4.2.1	<i>Momentum conservation (4.1a)</i>	77
4.2.2	<i>Heat conservation (4.1b)</i>	78

4.2.3	<i>Solute and mass conservation (4.1c,4.1d)</i>	78
4.3	Numerical implementation	78
4.4	Numerical Results	80
4.4.1	<i>Final considerations</i>	84
5	MULTI-DOMAIN MODELLING	85
5.1	Mathematical Formulation	85
5.1.1	<i>Solid region</i>	88
5.1.2	<i>Mush</i>	89
5.1.3	<i>Melt region</i>	92
5.1.4	<i>Boundary and interface conditions</i>	92
5.1.4.1	<i>Heat and solute</i>	92
5.1.4.2	<i>Mass</i>	93
5.1.4.3	<i>Initial conditions</i>	94
5.2	Nondimensionalization	95
5.3	Analysis	97
5.3.1	<i>Transformed equations</i>	97
5.3.2	<i>The limit as $\tau \rightarrow 0$</i>	99
5.4	Numerical Implementation	103
5.5	Results	104
5.5.1	<i>$R = 1$ and $\tau \rightarrow 0$</i>	104
5.5.2	<i>$R \neq 1$ and $\tau \rightarrow 0$</i>	105
5.5.3	<i>Non-similar problem: $\tau > 0$</i>	114
5.5.4	<i>Validation</i>	125
5.5.4.1	<i>Similarity Solution</i>	125
5.5.4.2	<i>Non-similar Solution</i>	126
6	CONCLUSIONS AND FUTURE WORKS	129
6.1	Summary	129
6.2	Originality	130
6.3	Significance	131
6.4	Unification	132
6.5	Future work	132
6.6	Acknowledgments	132
	BIBLIOGRAPHY	133
	APPENDIX A SMALL-TIME MODEL REPORT	143

APPENDIX B	NON-SIMILAR – THREE REGIONS	
	MODEL REPORT	145
APPENDIX C	NON-SIMILAR – TWO REGIONS	
	MODEL REPORT	147
APPENDIX D	PUBLICATIONS	149

INTRODUCTION

In Brazil there are eleven main metallic commodities of economic relevance that together were responsible for R\$ 129 billions in production value during 2019, according to the last Brazilian Mineral Yearbook, published by the National Mining Agency ([ANM, 2020](#)). Among aluminum, copper, chromium, tin, manganese, niobium, nickel, gold, vanadium and zinc, the iron ore held the largest share representing more than half of the mineral production nationwide, taking the country to the second position in the ranking of iron ore producing nations in that same year, according to US Geological Survey data ([USGS, 2020](#)), highlighting the importance of this mineral for the national economy and for the global production of steel.

The global crude steel production, in its turn, has been on a rise for the past decade, reaching 1,874.9 million tonnes (Mt) in 2019, and Brazil was responsible for more than a half of Latin America's production in the same period, occupying the 9th position in the world ranking with 32.5 Mt, representing \$ 7.3 billion in exports, according to Brazil Steel Institute.

The manufacturing process may be divided in two main groups, the conventional casting and the continuous casting, both process may be observed in Fig. 1.1. In conventional casting, the molten metal is teemed or poured from the ladle into one or several moulds, letting the metal cool and solidify before being removed from the mould. The melt may be poured from above into the mould, in a down-hill casting, or supplied from below, in a uphill casting as shown in Fig. 1.1 ([FREDRIKSSON; ÅKERLIND, 2006](#)).

In the continuous casting, a strand of solid metal is continuously drawn out from the vertical water-cooled chill-mould while it is continuously fed with new melt from above. The idea was firstly presented by Henry Bessemer in 1856, but it wasn't until the 1940s that it became a common production method in the casting of nonferrous metals and later from the 1960s for steels. The major advantages are, as presented in ([LOUHENKILPI, 2014](#)), improvement of steel quality, better yield, and savings of energy and manpower, since intermediate cooling times in moulds are drastically reduced.

In Brazil, the crude steel production by continuous casting added up to 31,803 Kt in 2019, as the conventional casting produced 598 Kt (AÇOBASIL..., 2020). Similar ratio may be observed worldwide, where about 95% of the global steel production today is manufactured by continuous casting process. Nevertheless, conventional casting is still essential to production of industrial components that include single parts with large dimensions and high production cost, such as pressure vessels – structures used to maintain a material at high pressure – necessary to the generation of nuclear energy (PICKERING, 2013).

According to Brazil Steel Institute, the national company Gerdau produced alone around 3.08 Mt of steel ingots, blooms and billets in the last three years, adding to the 4.38 Mt produced nationally.

In Europe, the Swedish company Ovako, a steel producer for customers in the fields of bearings, transport and manufacturing (OVAKO..., 2014a), even though relying heavily on continuous casting processes, uses the conventional casting to produce 4.2t ingots since it is the only accessible casting method for the production of some types of rolling steel. (OVAKO..., 2014b)

The Italian group FOMAS with production units in São Paulo, is a specialist in open die forging and bearing rings in steel, nickel and titanium alloys, consuming an average of 180 thousand tons of raw material per year. Able to manufacture ingots up to 125 tonnes to serve industries in the power generation and oil and gas industries. (FOMAS..., 2014)

ArcelorMittal, the largest steel and mining company in the world, produced, in 2013, 100.5 Mt of steel, of which 38 % were produced in the Americas and 46 % in Europe, the company has facilities for the manufacture of ingots used in production of railroad tracks, open die forging and other industrial applications. In addition, it also produces ingots for pressure vessels, in which steel must be able to withstand high pressure at different temperatures. (ARCELORMITTAL..., 2014)

In India, Vimal Alloys supplies steel ingots up to 6.1t (VIMALALLOYS..., 2014). Headquartered in England, Vesuvius also invests in casting ingots and uses patented technologies to reduce the effects of unwanted segregation and increase the

Figure 1.1 – Casting steps for metal alloys. Adapted from (OVAKO..., 2014b). The dashed red line shows the domain of the problem addressed.

quality of steel in the final product. (VESUVIUS..., 2014)

Despite being the most experienced method, the conventional casting products are still subject to many quality issues, such as gas porosity, shrinkage and segregation effects, among others. The macrosegregation in metal ingot casting – a phenomenon characterized by a severe variation on composition at the macroscopic scale – can significantly decrease the usability of the final product and due to the inherent complexity in its mathematical model has not been satisfactorily predicted by existing software.

As it is a topic of interest for the steel industry, considerable efforts have been made in the last 25 years to develop software for computational simulation that can predict the occurrence of macrosegregation. Although the underlying physics is well known (FREDRIKSSON; ÅKERLIND, 2006; FREDRIKSSON; ÅKERLIND, 2012), even software dedicated to foundry as casting processes such as MAGMASOFT® are unable to adequately predict segregation of type A (RAD; KOTAS; BECKERMANN, 2013), and do not present reliable results either quantitatively or qualitatively (PICKERING, 2013). As this phenomenon is primarily associated with the convection of liquid metal, there is a considerable scope for the improvement of macrosegregation modeling. As the ingot casting of steel is chosen as an example of this process along this text, it is also valid for other metals.

The growth of the mathematical model in terms of complexity is also a factor to be observed, as observed by Pickering in a review on macrosegregation developments during the 20th (PICKERING, 2013), the high demand for computational resources has sometimes led to the reduction of the modeled systems, decreased resolution in the meshes, and the introduction of major simplifications. Such simplifications would be common practices in commercial software aimed at casting processes, which would be done in order to provide numerical results with practical computing times for industrial applications (THERCAST, 2021; MAGMASOFT, 2021; PROCAST, 2021). Consequently, still according to the author, its results often provide little predictive understanding.

1.1 Ingot solidification

Ingot solidification occurs, according to (CARDOSO, 1995), by nucleation process and solid phase growth. The nucleation comprises the creation of crystallization nuclei (formed spontaneously or associated with the impurities of the material and mold walls), and the fixation of atoms neighboring this surface, resulting in the formation of the crystalline structure of the metal. These compositions made of primary grains are called dendrites and their growth stops when they encounter other crystallized compositions or when the liquid material runs out. As will be seen later, the composition of the liquid that permeates the dendrites will play a fundamental role in the formation of macrosegregation.

In order to better understand the formation of these structures, experimental schemes and

illustrations can be observed as presented in (FLEMINGS, 1974): when starting the solidification process, the planar interface becomes unstable and starts to show small undulations with protuberances that develop for cell structures, as shown in Fig. 1.2 in a transparent organic alloy.

In order to observe similar cellular structures in metal alloys, it is necessary to interrupt the solidification process quickly by means of a thermal shock, the result can be seen in Fig. 1.3. A cross-section for a similar structure is seen in Fig. 1.4, in which a pattern of cells developed in equally spaced cylinders with six faces resulting from joint growth is noted.

Figure 1.2 – Cell interface in transparent alloy (CBr_4 - tetrabromomethane). Adapted from (FLEMINGS, 1974)

Regular cells, as seen in Figs 1.2 - 1.4 occur when the growth velocity of the structures is relatively low inducing prolongation in the direction perpendicular to the liquid-solid interface, regardless of the metallic crystal orientation. However, when the growth rate is high, crystallographic effects start to act on the growth direction of the cells. Also according to (FLEMINGS, 1974), there is a simultaneous variation in the shape of the cell in its transverse portion that would be originally circular, as shown in Fig. 1.5. The illustration shows the transition from a circular cell to a flanged structure. In Fig. 1.5.a, the growth rate is low enough to maintain the structure of the cell, from Fig. 1.5.b, the cell then starts to grow towards the main crystal axis ($\langle 100 \rangle$ for cubic metals)

As in (FREDRIKSSON; ÅKERLIND, 2008), the orientation of the normal to the plane of a crystal can be uniquely defined by the three intersections between the plane and the coordinate axes as in Fig. 1.6, its identification is made here by the *Miller indexes*, a way of representing the orientation of a crystal in the form $(hkl) = \left(\frac{D}{X} \frac{D}{Y} \frac{D}{Z} \right)$, where $X = \frac{D}{h}$, $Y = \frac{D}{k}$, $Z = \frac{D}{l}$. hkl are the

Figure 1.3 – Fully developed cells in metallic binary alloy Al-Cu (aluminum and copper). Adapted from (FLEMINGS, 1974)

so called Miller indexes, (X, Y, Z) are the intersection coordinates between the plane and the coordinate system, calculated using the least common denominator $D = l.c.d\{X, Y, Z\}$.

The step in Fig. 1.5 in which the cell structure becomes dendritic is a matter of terminology: some authors consider it to be from the moment when the growth of the structure is influenced by the orientation of the crystal (Fig. 1.5.b), for others the term should be applied only when secondary branches become visible, as in (Fig. 1.5.d). In addition, the same illustration shows two discernible structures: the primary dendritic arm growing in the opposite direction to the heat flow; and the secondary dendritic arm, protrusions perpendicular to the primary dendritic arm. Following the nomenclature adopted in (FLEMINGS, 1974), primary dendritic arms originating from the same nucleus with the same crystallographic orientation are said to be parts of the same grain, or dendrite.

The creation of new crystallization nuclei, however, is not always linked to the occurrence of new nucleation, but to the phenomenon of grain multiplication, described in (FLEMINGS, 1974) as an important source of crystallization nuclei. For metallic ingots, this phenomenon would be caused by the re-melting of dendritic structures, as illustrated in Fig. 1.7, which shows the development stages of a dendrite. Redirection causes a reduction in the number of dendritic arms and, according to (FREDRIKSSON; ÅKERLIND, 2012), it can occur through several processes, including ripening, a mass transport process: the diffusion of a solute in the metallic alloy from a thinner secondary dendritic arm towards a thicker dendritic arm, as a result of this process the smaller structure disappears. The initial disposition of the secondary dendritic arms,

Figure 1.4 – Transversal slice on cellular structure in metallic binary alloy Pb-Sb (lead and antimony). Adapted from (FLEMINGS, 1974)

Figure 1.5 – Changes in the shape of the solidification structures by increasing their growth speed: (a) regular cell growing at low speed; (b) regular cell growing in the $\langle 100 \rangle$ direction; (c) flanged cell; (d) dendrite showing periodic lateral branches. Adapted from (FLEMINGS, 1974)

therefore, changes during growth, some become unstable and melt again, while others continue to grow.

Also according to (FREDRIKSSON; ÅKERLIND, 2012), the surface energy and the

Figure 1.6 – Intersection coordinates between the plane and the coordinate system. Adapted from (FREDRIKSSON; ÅKERLIND, 2008).

Figure 1.7 – Diagram for dendrite growth during solidification of an alloy. Adapted from (FLEMINGS, 1974)

curvature of the end of the dendrites play an important role in the melting process. One of the possible configurations for this event is illustrated in Fig. 1.8, in this case the intermediate secondary dendritic arm has a root that is thinner than normal, thus, the constitutional super cooling ¹ which was sufficient at the end of the dendrite to form its secondary arms, is reduced to a lower value such that the smallest radius of curvature can affect the melting point making it smaller in that region resulting in the melting of the lower portion and the separation of the secondary arm from the primary arm.

For (FLEMINGS, 1974), if the secondary arm is loaded into the interior slightly super cooled, a new crystal is formed without the addition of a nucleation event. Advectional transport, then, is shown as a powerful mechanism not only to carry away the detached arm, but also to dissipate heat by the liquid, so that the transported arm can grow after being displaced.

Figure 1.8 – Detachment of the secondary dendritic arm portion in relation to the original primary arm.
Adapted from (FLEMINGS, 1974)

Figure 1.9 – Convective flux on liquid and mushy zones during solidification process.

At the macro scale, it is also possible to verify the occurrence of convection in the liquid material for the conventional casting process, whose flow follows the patterns elicited in Fig. 1.9 and described as follows: initially, there is only liquid metal and allowing the cooling leads to the formation of a denser mushy zone in which the re-circulation is oriented in the opposite direction to that of the liquid region, so the process continues with the appearance of a solid

¹ Constitutional super cooling is caused by changes in both temperature and composition.

region from the borders of the ingot, eventually, there will only be the solid region and mush zone and, finally, the process will be complete with the existence of only the solid phase.

The mush zone, or *mushy zone*, is defined as the region in which the liquid and solid phases of the molten material coexist at various temperatures, with differences in concentration caused by the redistribution of the solute (KURZ; FISHER, 1992). Its occurrence as in Fig. 1.9 is denoted by the term “S + L” in Fig. 1.10 .

Figure 1.10 – Example of numerical solution considering Sn-10 % Pb alloy. The velocity field is computed on a two-dimensional domain and unidirectional solidification(a). It is also possible to see different lead concentrations across the solidified material (b). Adapted from (FREDRIKSSON; ÅKERLIND, 2006).

Macroseggregations are basically differences in concentration on a much larger scale than interdendritic spacing. They are defects whose formation and severity are sensitive to casting procedures and ingot size and fall into six categories: type A segregation, type V segregation, negative base segregation, Hot-top segregation, banding and inverse segregation, and the last three, as (PICKERING, 2013), are less recurrent in large ingots.

It is understood that the cause of the macrosegregation in ingots is, as in (FLEMINGS, 1974), the movement of the liquid and solid parts within the mush region. Highly segregated phases (high concentration differ-

Figure 1.11 – Differences in solute concentration (C) between the center and the side of the piece. Adapted from (FREDRIKSSON; ÅKERLIND, 2006).

ences) are found in this region during solidification, it is the physical displacement of these phases that induces macrosegregation.

This phenomenon is also important in continuous casting processes. As an example, Fig. 1.11 shows the variation in carbon concentration from the middle of the side surface to the center of a 10 x 10 cm billet in which the average concentration is 0.8 wt - % (percentage by mass), but exceeds 1.0 wt - % in the central portion.

In Fig. 1.12, at the top, we observe the formation of a shrinkage cavity; as soon as the molten metal is placed in the mold, the solidification process begins while the heat is transported out of the mold. According to (FREDRIKSSON; ÅKERLIND, 2006), the nucleation process then occurs on the walls, creating crystallization nuclei that will compose the solid phase that grows in the form of layers towards the interior of the ingot. The continuity of this process causes the surface of the metal that remains in the liquid phase to accumulate in the center of the ingot as it gradually descends, leading to a deformation that can take the shape of a “pipe” in the final product. The same mechanism is evidenced in Fig. 1.13 obtained from the experimental work using stearin ingots (BREARLEY; BREARLEY, 1918). The section of the ingot that contains the pipe cannot be used and must be discarded or remelt, incurring into extra costs of production. Understanding the mechanisms of its formation could help improving techniques to decrease the pipe height and, thus, being beneficial from the economic point of view.

Figure 1.12 – On the left and in the details are areas of occurrence of different forms of macrosegregation. On the right are represented the structures taken into account in the construction of models of multiple domains. Adapted from (PICKERING, 2013) and (FREDRIKSSON; ÅKERLIND, 2006).

Also in Fig. 1.12, the regions of occurrence of the different types of macrosegregation found in large ingots can be seen. The plus signs represent positive segregation, in which the concentration of a certain element of the metal alloy exceeds the average concentration. One can also observe the patterns reassembling the letters “A” and “V” that give the name to the A-segregation and V-segregation, respectively. Minus signs, in turn, denote negative segregation, where the local concentration is less than the average concentration.

Figure 1.13 – Photographed cross-sections of stearin ingot showing the pipe formation. Adapted from (BREARLEY; BREARLEY, 1918).

The type A segregation, according to (FREDRIKSSON; ÅKERLIND, 2006), is caused by the natural phenomenon of convection in the liquefied metal during its solidification process, which in turn occurs by varying the density and results in macrosegregation of the material.

This form of segregation is a source of concern for pressure vessel manufacturers: these vessels are created by removing the inner part of the ingots, followed by fixing metal parts by means of welding. But the integrity of welds can be impaired if they coincide with stretches of type A segregation, since this form of macrosegregation is commonly associated with increased hardness and reduced material toughness. (MAIDORN; BLIND, 1985)

The formation of type A segregation comes, more precisely, from the convective flow of solute-rich interdendritic fluid. In this case, convection is caused by the density gradient associated with changes in temperature and composition. Such thermal and compositional fluctuations can interact or oppose each other, if the local temperature and concentration field cause the liquid density to increase or decrease. (PICKERING, 2013)

Also according to (PICKERING, 2013), the formation mechanism of type A segregation can be detailed as follows: during the solidification of the steel, the enriched interdendritic fluid sometimes has a density lower than that found inside the liquid phase and tends to rise. While this portion of the interdendritic liquid moves towards the top of the ingot, its temperature will rise, but its composition will be practically constant due to the low mass transfer of the diffusive phenomenon. This warmer and enriched liquid will cause retarded growth and a new melting of the solid portion around it, causing in the final material the occurrence of solute-rich channels.

Type A segregation is related to the emergence of *hot-top* segregation. In this category,

Figure 1.14 – Comparison between the dimensions of ingots, macrosegregation defects and interdendritic spacing. Adapted from (COLPAERT; SILVA, 2008).

positive segregations are observed near the top of the ingot and are caused mainly by convection in segregation channels type A (FREDRIKSSON; ÅKERLIND, 2006). According to (PICKERING, 2013), if the decrease in temperature on the upper face of the ingot is sufficient to lead to the solidification of the material, then the dendritic boundary will advance towards the base. In this process, a portion of liquid enriched in solute and at a relatively low temperature can flow and enrich the liquid below the surface. In the first moments of solidification, this liquid with the highest concentration will mix with the rest of the material, but in the final moments it will remain in the center of the upper portion of the ingot, as seen in Fig. 1.12. Fig. 1.14 illustrates the order of magnitude of inter-dendritic spacing compared to the dimensions of ingot casting.

1.1.1 Phase Diagrams

In this section we are going through some concepts around phase diagrams and phase transformations that are going to be referred to when defining the boundary conditions and exploring the nature of eutectic/non-eutectic solidification.

Phase diagrams are a symbolic representation that contains summarized information of

Figure 1.15 – Phase diagram of binary eutectic system

alloy on diverse composition and phases as a function of temperature, where the concentrations of its component is presented on the X-axis and the temperature on the Y-axis, as the one presented in Fig. 1.15. Consulting these diagrams allow us to get the approximated temperature at which the phase transitions occur. The regions separated by the lines represent different phases, while the line that bounds them constitute the equilibrium conditions.

Figure 1.16 – Phase diagram of binary non-eutectic system

According to (FREDRIKSSON; ÅKERLIND, 2012), minor changes on the temperature may easily induce the creation of a new phase or lead to the disappearance of an existing one in a process called phase transformation or phase reaction. Such transformations may involve a different number of reactant which can be categorized in four different groups, as presented on Table 1. In this table, the three first reactions involve only one reactant, while the Peritectic reaction type involves two reactants.

Back in Fig. 1.15 we can observe the phase diagram for a binary alloy under eutectic phase transformation. Here the liquid phase L may simultaneously precipitate into one or two solid phases α , β , or $\alpha + \beta$, the different phases have distinct micro-structures and that may

Name of reaction	Reaction when cooled	Phase diagram
Eutectic	$L \rightarrow \alpha_{\text{solid}} + \gamma_{\text{solid}}$
Monotectic	$L_1 \rightarrow L_2 + \gamma_{\text{solid}}$
Metatectic	$\beta_{\text{solid}} \rightarrow \alpha_{\text{solid}} + L$
Peritectic	$\alpha_{\text{solid}} + L \rightarrow \beta_{\text{solid}}$

Table 1 – Tectic type reactions. Adapted from (FREDRIKSSON; ÅKERLIND, 2012)

largely affect the final material properties. The horizontal line at the eutectic temperature T_{eut} , delimits a constant value below which all the liquid phase vanishes. If the temperature decreases in a melt having eutectic composition, no solid phase is precipitated until the temperature has reached the eutectic temperature. An eutectic alloy is defined as a binary alloy with a composition that corresponds to the eutectic point in the phase diagram. Similar phase diagrams are found in the two most frequently used cast alloys, silumin and cast iron, among a number of metallic and ceramic systems of commercial interest (FREDRIKSSON; ÅKERLIND, 2006).

The material that solidifies having eutectic composition precipitates into two solid phases with compositions x_{α} and x_{β} at the constant proportions N_A and N_B , respectively, that are presented in eq. (1.1) and correspond to a constant chemical composition x_{eut} . The rates a and b express the difference between the eutectic composition and the highest composition in the phase α and the lowest composition in phase β . The solidification process is then called a eutectic

reaction.

$$\frac{N_A}{N_B} = \frac{b/(a+b)}{a/(a+b)} = \frac{b}{a}. \quad (1.1)$$

In the monotectic reaction, instead of precipitating into two solid phases, the liquid gives a solid phase γ_{solid} and another liquid phase L_2 . The metatetic reaction, in its turn, can be understood as a mixture of a peritectic and a eutectic reactions, where a primarily precipitated phase β_{solid} decomposes into a new solid phase α and a liquid phase L . A peritectic reaction occurs when a melt reacts with a primarily formed phase α forming a secondary phase β .

In this diagrams, the horizontal axis usually stands for the concentration of solute, i.e. the material that take up a smaller portion of the alloy. While in Fig. 1.16 we can see a different phase diagram corresponding to alloys like Cu-Ni, where the horizontal axis shows the concentration that ranges from x_c to x_d where the extremes represent pure materials, e.g. pure copper or pure nickel, and T_c and T_d correspond, respectively, to its solidification temperature. Similar phase diagram can be found for Ag-Au alloy.

1.1.2 The Mullins-Sekerka Instability

First studied in 1964, the Mullins-Sekerka instability (MULLINS; SEKERKA, 1964), considers an unidirectional freezing of a dilute binary alloy and theoretically investigates the stability of the moving planar liquid-solid interface. The methodology is to introduce an arbitrary sinusoidal perturbation of infinitesimal initial amplitude into the shape of the plane and to calculate the time dependency on the perturbation amplitude. That perturbation was analyzed using infinitesimal sinusoidal Fourier components, the superposition of those components developments can reveal the origin of the perturbation itself. If any sinusoidal wave is found to grow on the plane, the moving planar interface is considered unstable, otherwise it is said to be stable.

The physical assumptions on the study are the isotropic parameters on bulk and surface, and local equilibrium at the interface. The analysis of the planar interface reveals that the stability depends on three factors: the first arising from capillarity; the second relating to the thermal gradients; and the third representing the effect of solute on the equilibrium melting temperature. The first two favors the decay whilst the third favors the growth of the sinusoidal wave. Consequently, the instability occurs when the magnitude of the third term exceeds that of the sum of the first two terms.

1.2 Contributions

This research was developed in three fronts: the first tackles the shrinkage cavity formation during the solidification in conventional casting; the second is dedicated to the implementation of a two-dimensional, transient, single-domain mathematical model capable of predicting the occurrence of macrosegregation; in the third, a one-dimensional, transient, multi-domain model

is presented together with the corresponding similarity solution valid for the earlier moments of the solidification process, as well as the numerical solution for the full non-similar problem. From the three fronts the following contributions can be summarized:

- The cavity computed in the first part of this work has its consistency verified by the balance of mass, where the absent area compensates the density variation between the liquid and solid phases. An apparatus used in the industry to prevent its formation is numerically tested;
- For the two-dimensional, single-domain model, a satisfactory prediction of the occurrence of the macrosegregation was obtained, when compared to existing numerical data available in the literature. The results achieved in this topic have been published ([ASSUNÇÃO; VYNNYCKY, 2018](#)) and may form the basis for new studies that include a three-dimensional model or more complex metal alloys.
- The similarity solution for the one-dimensional problem is validated against results available in the literature. Part of this work, more specifically, the discussion around the similarity solution for small times has been published ([ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020](#)), while the advances on the full non-similar problem are in preparation and should complement the previous paper ([ASSUNÇÃO; VYNNYCKY, 2021](#)). Beyond establishing a framework to more complex models, these results may also serve as benchmark for the testing of numerical codes developed in the area.
- The one-dimensional model extends the existing models in the literature to the more general situation of a finite spatial domain, arbitrarily large superheat and both eutectic and non-eutectic solidification constituting the correct initial condition for the subsequent numerical solution of the full non-similar problem whose results are also presented in this thesis.
- Using the one-dimensional model, it was possible to study the effects of several parameters on the final macrosegregation profile, leading to creation of guidelines that could theoretically help to reduce the standard deviation in solute composition by up to 40%.

1.3 Outline

A Literature Review is presented in Chapter 2, where the first Section is dedicated to describing the Amberg's work ([AMBERG, 1991](#)) on building a two-dimensional transient mathematical model with a single set of equations valid throughout the domain, including aspects regarding to constitutive relations supported by ([INCROPERA; DEWITT, 1985](#)), and physical interpretation provided by ([FREDRIKSSON; ÅKERLIND, 2006](#)).

Later, we enumerate the many aspects involved in the multi-domain formulation and how they were contemplated by different works in the literature starting from the developments of the pioneer Flemings and co-workers (FUJII; POIRIER; FLEMINGS, 1979), touching the work of Szekely and Jassal (SZEKELY; JASSAL, 1978), and arriving at the semi-infinite model developed by Voller (VOLLER, 1997).

After that, the basic theory on Stefan problems, a demonstration of similarity transformation and a brief description of Arbitrary Lagrangian-Eulerian method are presented. The similarity transformation will be essential to operate the resulting system of differential equation in multi-domain modelling, where the movement of the interfaces is approximated using the Stefan conditions to be solved with the aid of the ALE method.

In Chapter 3, we formulate a 2D transient mathematical model for the formation of central cavity induced by the density differences during the solidification process. The temperature and the cavity shape are solved using the commercial software Comsol Multiphysics together with an in-house script developed in Matlab and communicating through LiveLink for Matlab. The numerical results obtained from the model are then compared with those provided by Raihle and Fredriksson (RAIHLE; FREDRIKSSON, 1993).

In Chapter 4, the 2D transient model based on Amberg's work is summarized and nondimensionalized resulting in a set of equations to be solved numerically for temperature, solute concentration and liquid fraction considering the casting of Fe-C steel ingots, using a Marker and cell Method coded in Matlab. Later, a study is carried out in order to understand the limitations posed by an arbitrarily defined numerical parameter ε and its effects on the elevated computing requirements.

In Chapter 5, a novel finite one-dimensional model is proposed with three distinct regions (multi-domain approach) including the temperature, solute concentration, liquid fraction and moving interfaces as the unknowns. Thereafter, a triple Landau transformation allows us to obtain a semi-analytical solution with the aid of Comsol Multiphysics, the results are in turn employed as the initial condition for the transient one-dimensional model valid throughout the solidification process, considering an Al-Cu binary alloy.

Moreover, a parameter study is carried out in order to understand the effects of density ratio, superheat, cooling boundary temperature and assumptions regarding solute transport at the microscale (Scheil or lever rule), on temperature and liquid fraction profiles, convective flow, growth of solid and mush regions, and, finally, the macrosegregation profile. With that data it is ultimately possible to dispense some guidelines on how to mitigate the macrosegregation defect.

In the final Chapter 6, the concluding remarks are summarized based on Chapters 3–5, and some perspectives for future works are presented.

LITERATURE REVIEW

The mathematical modelling of shrinkage cavity (or pipe formation) in ingots produced by conventional casting, or even metal billets in continuous casting, started with the work of Fredriksson and other researchers (BROLUND *et al.*, 1986), (RAIHLE; FREDRIKSSON, 1994), (ENGSTROM; FREDRIKSSON; ROGBERG, 1983). The mathematical modelling of macrosegregation started with the work of Flemings and other researchers (FLEMINGS; NEREO, 1967), (FLEMINGS; NEREO, 1968a), and (FLEMINGS; NEREO, 1968b). In this series of papers, macrosegregation was studied analytically and experimentally. According to (PICKERING, 2013), there are basically two approaches to the mathematical modeling of macrosegregations, which result in multi-domain models or continuous models. In the first approach, equations of conservation of mass, solute, momentum, and energy are developed for each domain: liquid, mush, and solid. The domains interact with each other and are bounded by moving interfaces. In this case, the dynamics of the liquid phase is typically described by the Navier-Stokes equation for convective laminar flow, and the Darcy equation for the mush zone.

In the second approach, a single set of equations is formulated that is equally valid for all regions. This removes the difficulty found in multi-domain models to trace the moving boundaries that can take complex shapes throughout the simulation. For that, it is generally used the modified Navier-Stokes equation by adding terms to take into account the resistance caused by solid portions in the mush zone.

Some of the most significant works in pipe formation is presented in Section 2.1, while advances on single domain approach is presented in Section 2.2, and the configuration with multiple domains and its many aspects is discussed in Subsection 2.3. Latter, three topics of investigation are briefly described, as they have been proved useful at different stages of studying solidification problem, to be applied to the mathematical formulation, analytical solution or the numerical solution. These subjects are of great importance specially when dealing with the multi-domain model: the Stefan problem presented in Section 2.4, the Similarity solution in Section 2.5 and the Arbitrary Lagrangian-Eulerian method in Section 2.6.

2.1 Pipe formation modelling

The earliest attempt in understanding the mechanism of pipe formation was carried out over a hundred years ago by the metallurgists brothers Arthur and Harry Brearley of Brown-Bayley's Steel Works Limited. The pipe formation was considered among a number of aspects concerning the casting methods and the results were summarized in the book of their authorship (BREARLEY; BREARLEY, 1918). Harry Brearley – regarded as the inventor of stainless steel – collected experimental data on the formation of pipes in stearin ingots which were decanted for different periods of time before being sectioned, as the authors sketched the first attempts in describing the phenomenon. Their observations would motivate researchers to develop pioneering works in the subject, some of which are hereinafter summarized.

2.1.1 Fredriksson and co-workers

Inspired by the works of Brearley, mathematical models on pipe formation were elaborated by Fredriksson and co-workers later in the 80s. In (BROLUND *et al.*, 1986), two models were derived to calculate the pipe shape: in the first approach, a model describes the pipe formation in an ingot without a hot-top; in the second, the solidification process is analyzed considering the existing hot-top of the ingot as an independent part in a model that is based on volume balance and on the difference in solidification rate between the top portion and the rest of the ingot.

In an ingot without the hot-top, the mass balance is used to derive an analytical expression for the shape of the pipe, written as

$$\rho_l A dz = (\rho_s - \rho_l) dV, \quad (2.1)$$

where ρ_s and ρ_l are the density of solid or liquid material, A is the area of liquid at the top, dz is the distanced moved by the top surface, and dV is the volume of solidified material. For the ingot with the hot-top, where the solidification is much slower, the model accounts for two volumes, one in the ingot and one in the top, and the mass balance becomes

$$\rho_l A_b dz_b = (\rho_s - \rho_l) (dV_b + dV_{ig}), \quad (2.2)$$

where the subscript b refers to the hot-top volume, while the ig stands for the ingot portion.

Instead of recurring to numerical methods to carry out the computational simulation of the solidification processes, the authors proposed a set of analytical expressions incorporating the assumption that the two volumes can be considered separately with the geometry expressed in Fig. 2.1 from which expressions are derived for A_b , dV_b , dV_{ig} , the solidification rate in the hot-top and from the bottom can be related to the solidification rate of the ingot with the relations

$$n = \frac{dx_b}{dx_{ig}}, \quad m = \frac{dz_{ig}}{dx_{ig}}, \quad (2.3)$$

arriving at the relation for the pipe depth $e = z_b/z_b^0$ with

$$e = x_b^{2\beta} C + \frac{\beta}{2nz_b^0} \left(\frac{3vx_b}{n^2(1-2\beta)} - \frac{2(K+\mu)}{\beta n} - \frac{\mu(4K+\mu)}{x_b(1+2\beta)} \right), \quad (2.4)$$

where the superscripts ⁰ denote the initial values, and C is determined by the relations $e = 1$, $x = x_b^0$.

The solution found in eq. (2.4) is valid for a square ingot, while a similar expression for cylindrical ingots were also derived in the paper. However, they are limited to non-conical ingots, the heat loss from the upper surface is neglected nor is taken into account the effect of macrosegregation on the height of the hot-top. The authors attempt to develop a model that could help optimizing the usable portion of ingots, in fact, the final geometry is the only solution obtained from the equations since the model does not account for heat or mass transfer.

Figure 2.1 – Ingot and hot-top geometry. Extracted from (BROLUND *et al.*, 1986).

Although the pipe formation is usually associated with ingot casting and normally disregarded in continuous casting of steel, the defect frequently occurs at the end of a casting sequence, in the last portion of the solidified strand. In (RAIHLE; FREDRIKSSON, 1994), the effects of cooling and casting conditions on the centerline macrosegregation and size of the pipe are discussed for continuously cast billets.

During the continuous casting, the liquid is supplied to the mold to compensate for the volume decrease until the end of the operation, when the feeding of liquid metal ceases. At this moment, similarly to what happens in conventional ingot casting, contraction and volume changes causes a decrease in liquid volume, decreasing the liquid surface level at the top of the product and creating a cavity.

Figure 2.2 – Volume balance displaying the liquid surface and the position of the solidification front at times t and $t + dt$. Adapted from (RAIHLE; FREDRIKSSON, 1994).

In (RAIHLE; FREDRIKSSON, 1994), the earlier model presented in (BROLUND *et al.*, 1986) was adapted in order to solve for the pipe formation in continuous casting by including the effects of thermal shrinkage. The model is also based on material balance and is explained using Fig. 2.2: the volume dV_s solidifies during the time dt , causing a certain volume to disappear resulting in a volume dV_c and moving the liquid pool surface by dh . Thus, the differential material balance is expressed as

$$\frac{dh}{dt} A_s = \frac{dV_s}{dt} \beta + \frac{dV_c}{dt}, \quad (2.5)$$

where A_s is the area of the metal liquid surface, β is the solidification shrinkage coefficient

$$\beta = \frac{\rho_s - \rho_l}{\rho_l}, \quad (2.6)$$

with ρ_s , and ρ_l representing the density of solid or liquid material. The left-hand side describes the change in depth of the pipe, on the right-hand, the first term side describes the contribution due to solidification shrinkage and the second denotes the contribution due to thermal contraction.

The contribution due to solidification shrinkage is determined as

$$\left[\frac{dV_s}{dt} \right]_t = \int_{z=h}^{z=L_0} l_1 \frac{dy}{dt} dz, \quad (2.7)$$

where l_1 is the length of the periphery of the solidification front, and y , h , L_0 are defined in Fig. 2.2.

The temperature profile is obtained by solving the Fourier's heat equation in two dimensions. However, the pipe formation may also suffer the influence of alloy composition, thermal

expansion coefficient, thermal conductivity, latent heat, heat capacity and thermal contact resistance between the mold and the steel surface. All those effects have been neglected in (RAIHLE; FREDRIKSSON, 1993).

2.1.2 Radovic et al (RADOVIC et al., 2010)

In a more recent study, the influence of melt temperature, alloy composition and temperature gradient on the shrinkage intensity in steel ingots are numerically studied (RADOVIC et al., 2010). The material balance is used to calculate the change of volume during solidification

$$\frac{dh}{dt}A_{sl} = \frac{dV_s}{dt}\beta + \frac{dV_c^s}{dt} + \frac{dV_c^l}{dt}, \quad (2.8)$$

where h is the pipe height, A_{sl} is the boundary area of liquid and solid, dV_s/dt is the solidification shrinkage, β is a solidification shrinkage coefficient, as used in (RAIHLE; FREDRIKSSON, 1994), dV_c^s/dt is the volume change caused by thermal contraction, and dV_c^l is the volume changes of liquid during cooling.

Following (RAIHLE; FREDRIKSSON, 1994), the volume change in the first term of the right-hand side of eq. (2.8) is determined by

$$\frac{dV_s}{dt} = \int_0^V \left(\frac{d\phi}{dT} \frac{dT}{dt} \right) dV, \quad (2.9)$$

where ϕ is the solid fraction assumed to behave as an *ad-hoc* function of temperature T

$$\frac{d\phi}{dT} = \frac{1}{(T_l - T_s)(1 - 2/\pi)} \left(1 - \sin \left(\frac{\pi}{2} \left(\frac{T - T_l}{T_s - T_l} \right) \right) \right), \quad (2.10)$$

depending on the liquidus and solidus¹ temperatures T_l , T_s . Following (ENGSTROM; FREDRIKSSON; ROGBERG, 1983), the thermal contraction in the second term of the right-hand of eq. (2.8) is defined as

$$\frac{dV_c^s}{dt} = \int_0^h \int_0^s \left(2\lambda \frac{dT(x)}{dt} (s-x) - 2\lambda \frac{(s-x)^2}{s} \frac{dT_s}{dt} \right) ds dh, \quad (2.11)$$

where s is the half of the ingot section, x is the distance from the ingot surface, λ is the thermal expansion coefficient, dT_s/dt is the cooling rate of the surface and $dT(x)/dt$ is the cooling rate at the position x .

The last term in eq. (2.8) describes the liquid thermal contraction during cooling as

$$\frac{dV_c^l}{dt} = \frac{dT_{liq}}{dt} V_l \delta_l, \quad (2.12)$$

where δ_l is the liquid thermal expansion coefficient and V_l is the liquid volume. Eqs. (2.8–2.12) are used to solve for the pipe height, while the temperature profile is modelled using a

¹ NB: liquidus temperature is the lowest value at which the material is completely in the liquid phase. Likewise, solidus temperature is highest value at which the material is completely solid.

two-dimensional Fourier's differential equation, with boundary conditions characterizing the steel ingot solidification process. A square cross-section was considered by the authors with assumed symmetry in a direction along the ingot centreline, allowing a quarter of the ingot cross-section to be taken as a representative area. With the assumptions, the equations are reduced to a one-dimensional, transient problem before being solved numerically.

Moreover, the model does not study the influence of the hot-top on the solidification process and, while the temperature profile is necessary to calculate the shape of the pipe at each moment t , the deformation caused by the cavity growth cannot alter the spatial domain in which the heat transfer is defined. One of the consequences of the approach is that as the spatial domain remains unchanged, the initial mass is not preserved, which may have a significant influence on temperature profile throughout the simulation. The effect is minimized by setting a heat transfer coefficient that causes the calculated temperatures to fit the experimental data.

2.2 Single domain modelling

In this section the work of Amberg (AMBERG, 1991) is described in detail, a single domain model is formulated based only on fundamental laws of conservation of mass, momentum, heat, and solute conservation, in addition to thermodynamic relationships that govern the change of phases. Aspects regarding to constitutive relations are supported by (INCROPERA; DEWITT, 1985), while the considerations on physical interpretation of parameters are helped by (FREDRIKSSON; ÅKERLIND, 2006). As previously mentioned, the solidification process generates three distinct regions: solid, liquid and mush, and a single set of equation must be valid for all of them.

2.2.1 Momentum conservation

The velocity field can be obtained from the linear momentum balance so that it is valid in all three regions:

$$\rho_0 \frac{D\mathbf{u}}{Dt} - \mu \nabla^2 \mathbf{u} = -\nabla p - \rho g \mathbf{e}_y - \frac{\mu}{H(\chi)} \chi \mathbf{u}.$$

Where D/Dt denotes the material derivative or Eulerian derivative operator:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla,$$

leading to:

$$\rho_0 \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) - \mu \nabla^2 \mathbf{u} = -\nabla p - \rho g \mathbf{e}_y - \frac{\mu}{H(\chi)} \chi \mathbf{u}. \quad (2.13)$$

In addition, the melt density can be written as a function of carbon concentration and temperature for a Fe-C alloy following the correlation

$$\rho = \rho_0(1 + \alpha'(T - T_0) + f \cdot c_l), \quad (2.14)$$

where T_0 denotes a reference temperature corresponding to the melting point of pure iron (0 wt% carbon), and $\alpha' = \frac{d}{e + 100c_l}$ with the coefficients determined in the experimental work of Olsson (OLSSON, 1980).

Note on the right side, the terms corresponding to Darcy's law, which governs the flow in a porous medium. In addition, in the eq. (2.13), ρ_0 denotes density in $[\text{kg/m}^3]$ referring to the initial state of the liquid, while the local density ρ can be written as a function of temperature and concentration measured in a given region of the domain, this relationship will be described later. The vector $\mathbf{u} = (u, v)$ denotes the velocity in the x and y directions of the coordinate axis being given in $[\text{m/s}]$, the velocity in the mush region can be understood as an average of the velocities through the porous medium. μ represents the dynamic viscosity in $[\text{Ns/m}^2]$. The pressure p is considered in $[\text{N/m}^2]$, g is the acceleration due to gravity (9.8 m/s^2), χ represents the liquid fraction, that is, it refers to the portion not yet solidified within a volume, ranging from 0 (solid) to 1 (liquid).

As can be seen in Fig. 1.14, the dimension of the dendrites has a scale of 0.1mm. This allows the mush region to be treated as a porous medium. In this context, the permeability variable $H(\chi)$ is used, which measures, according to (FREDRIKSSON; ÅKERLIND, 2006), the liquid's ability to penetrate through the dendrites of a region whose solidification process has started. The higher its value, the more easily the liquid can enter or leave a certain volume.

In (WEST, 1985), expressions are presented to describe the permeability as a function of the liquid fraction χ in the mush zone of metal alloys, which have yielded satisfactory results when compared against experimental data, as shown in Fig. 2.3, accordingly

$$H(\chi) = Z_1 K_1 + Z_2 K_2, \quad (2.15)$$

where $K_1 = \chi^2$, and

$$K_2 = \begin{cases} 0, & \text{if } \chi < \frac{1}{3}, \\ (1 - \chi)^{(2/3)} \left(3 + \frac{4}{1 - \chi} - 3\sqrt{\frac{8}{1 - \chi} - 3} \right), & \text{if } \chi \geq \frac{1}{3}. \end{cases} \quad (2.16)$$

The parameters Z_1 and Z_2 are constants obtained from experiments conducted by (PIWONKA; FLEMINGS, 1966), in that work the obtained values were $Z_1 = 6.4 \times 10^{-9} \text{ cm}^2$ and $Z_2 = 8.8 \times 10^{-7} \text{ cm}^2$.

In this case, it is noted that if the solidification process has not started in a certain region ($\chi = 1$), then the last term in the eq. (2.13) is neglected, leaving the usual equation of Navier-Stokes. When the solidification starts, the term gains importance in the equation, while the velocity tends to zero making the terms on the left side of the equation negligible.

Figure 2.3 – Permeability vs liquid fraction, squares represent experimental data and the solid line represents the results obtained from permeability equation. Adapted from (WEST, 1985)

2.2.2 Heat conservation

As in (AMBERG, 1991), it can be assumed that in a given volume of the mush region the temperatures of the solid phase and the liquid phase are in equilibrium, as long as the time necessary for thermal diffusion to take place through the distance of a pore is reasonably small. In this way, any temperature variation within the length scale with the same magnitude as an interdendritic spacing would be smoothed out quickly. Therefore, heat conservation can be modeled in terms of a single temperature T valid for the liquid, mush and solid regions:

$$\rho_0 c_p \left(\frac{\partial T}{\partial t} + \chi \mathbf{u} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) - \rho_0 \Delta H_f \frac{\partial \chi}{\partial t}, \quad (2.17)$$

where c_p represents specific heat, a physical quantity that defines the thermal variation of the material when absorbing a certain amount of heat, usually expressed in [J/(kg K)], k is thermal conductivity [W/(m K)] and represents the ability of a given material to conduct thermal energy. ΔH_f given in [J/kg] is the latent heat of fusion which indicates the amount of heat that a unit of mass of a certain material must receive to change phases from solid to liquid.

These thermophysical properties of the material are commonly found in the analysis of heat transfer problems in expressions such as ρc_p which describes the *volumetric heat capacity* and indicates the material's ability to store energy. According to (INCROPERA; DEWITT, 1985), high density substances are typically characterized by low specific heat, solids and liquids that are good media for heat storage have thermal capacity around $\rho c_p > 1 \text{ MJ}/\text{m}^3 \text{ K}$.

Another recurring term in this type of analysis is the thermal diffusivity coefficient $\alpha = \frac{k}{\rho c_p}$, the ratio between conductivity and thermal capacity. Also according to (INCROPERA; DEWITT, 1985), high diffusivity values indicate that a given material responds quickly to thermal changes in the environment in which they are inserted, while materials with a low

coefficient α respond more slowly and, therefore, take more time for the temperature profile to reach a steady state. However, the conductivity k varies considerably according to the state of the material, its value can be approximated as in (AMBERG, 1991), taking into account the liquid fraction χ present in a given volume, by the expression:

$$k = \chi k_l + (1 - \chi) k_s, \quad (2.18)$$

where k_l and k_s represent the thermal conductivities in the liquid and solid states, respectively.

2.2.3 Mass and solute conservation

In (AMBERG, 1991), it is assumed that the solid and liquid metal are incompressible, neglecting the shrinkage resulting from the solidification process and in accordance with Boussinesq's approach used in the momentum equation. For certain alloys, the increase in density as the material solidifies can be up to 20% of its original value. Even so, mass conservation is reduced to:

$$\nabla \cdot (\chi \mathbf{u}) = 0. \quad (2.19)$$

The transport of solute (carbon) within a binary alloy can be modeled by the advection-diffusion equation. The particularity for this case, in relation to the equation that determines the temperature T , is that here the diffusion coefficient is much lower than that of the temperature (around $10^{-9} \text{ m}^2/\text{s}$), and it cannot be argued that the concentration of solute in a dendritic arm is necessarily in equilibrium with the liquid phase surrounding it.

According to (AMBERG, 1991), there are two opposite approaches: in the first, rapid diffusion in dendrites is assumed, causing essentially uniform composition; another possibility would be to neglect diffusion in the solid resulting in a model where determining the concentration on the surface of the dendrite is done by using the composition of the interdendritic liquid only.

The first approach is linked to Scheil equation, while the second refers to the lever rule, the latter is valid only when there is rapid diffusion of alloy components in both the solid and liquid phases. Such forms are mathematically represented by:

$$c_l = c_l^0 \chi^{-(1-k_p)}, \quad \text{Scheil equation} \quad (2.20)$$

where c_l represents the current concentration of the solute in the liquid phase of the metal alloy, while c_l^0 denotes the concentration for the initial state, c_s represents the concentration of solute in the solid phase, and k_p represents the partition constant expressed as the ratio: $k_p = c_s/c_l$.

$$c_l = \frac{c_s}{k_p} = \frac{c_l^0}{\chi(1-k_p)}. \quad \text{Lever rule} \quad (2.21)$$

But in practice, as in (FREDRIKSSON; ÅKERLIND, 2006), the most viable option would be to use an intermediate form for the two relations between the extremes of rapid diffusion in the solid phase, or without any diffusion at all.

Another difficulty in modelling the solute concentration is the difference in solubility among the different regions of the domain during the solidification process, that is, the ability of the metal alloy to dissolve the solute depends on its physical state. Therefore, it is essential, in this set of equations, to handle the composition of the liquid phase c_l , and the composition of the solid phase c_s separately. For practical purposes, Amberg defined the mixture composition as in (AMBERG, 1991):

$$c_m = \chi c_l + (1 - \chi) c_s, \quad (2.22)$$

where $c_s = k_p c_l$. Which means the assumption of a rapid diffusion in the dendrites is incorporated into the model, according to the lever rule. The mass conservation on solute is then obtained as:

$$\frac{\partial c_m}{\partial t} + \nabla \cdot (\mathbf{u} \chi c_l) = D \nabla^2 c_m, \quad (2.23)$$

for the diffusion coefficient D . In absence of convection and diffusion it can be verified that c_m is a constant, as it would be expected from using the lever rule.

The liquid fraction χ found in the formulations above refers to the portion occupied by liquid, while its complement $(1 - \chi)$ represents the solid portion present in the same volume. This parameter allows us to build interpolating relations in the mush region. Also, Amberg determines that the temperature on the interfaces between solid and liquid phases, i.e. on dendrite surfaces in the mush, must follow the liquidus line on the phase diagram,

$$T = T_l(c_l), \quad (2.24)$$

approximated by a linear function

$$T_l(c_l) = T_0 - m c_l, \quad (2.25)$$

where T_0 is the melting temperature of pure iron, and m is the constant of proportionality or the liquidus line slope, and T_l is the melting temperature of the material, which depends on a given solute concentration at the liquid phase (c_l).

Looking at eq. (2.24) and eq. (2.25), we observe that the two unknowns are algebraically coupled and that compromises the mathematical nature of the expected differential equation system. At this point, Amberg decided to replace it by the admittedly arbitrary relation

$$\frac{\partial \chi}{\partial t} = \frac{1}{\varepsilon} (T - T_l(c_l)), \quad (2.26)$$

where the parameter ε allows the deviations on the eq. (2.24) to induce the solidification and restore T to T_l , where a smaller value for ε results in a faster solidification process. The equation consists in a simple way to solve for the liquid fraction χ .

With the parameter ε being proportional to the error in $T - T_l = 0$, eq. (2.25) can be satisfied to any desired degree of accuracy simply by choosing a value of ε small enough. However, eq. (2.26) limits the search for the suitable value of ε by determining that its minimal

allowable value must not be smaller than the time step used in the temporal discretization of the differential term, in order to guarantee its numerical stability. (AMBERG, 1991)

Moreover, it is numerically possible for χ to increase beyond 1 and decrease below 0, in that case the numerical implementation must interfere with the modelling to guarantee that any value of χ out of that range must be taken to be 1 or 0, respectively.

2.2.4 Boundary conditions

The model for the velocity field must usually incorporate the non-slip condition:

$$u = v = 0, \quad (2.27)$$

which simply means that the alloy velocity near the mould walls are negligible.

The boundary conditions for temperature may vary depending on the hypotheses made by each author, in (AMBERG, 1991), a constant heat flow Q [W/m²] was applied together with Fourier's law forming the Neumann boundary condition used to define the heat exchange on the ingot surface, in the form:

$$-k \frac{\partial T}{\partial \mathbf{n}} = -Q, \quad (2.28)$$

where $\mathbf{n}$ represents the normal vector at the boundary on which the boundary condition is applied. Other authors, however, impose a more detailed condition involving heat transfer through the mould walls and consider the formation of an air layer between the ingot and the mould which has an adverse effect on the efficiency of the solidification process. This layer of air, as revised in (VYNNYCKY, 2009) and specified in (SCHWERDTFEGGER; SATO; TACKE, 1998), (KRON *et al.*, 2004) and (FREDRIKSSON; ÅKERLIND, 2006), is formed when the outer layer of the solidifying metal, on passing from the plastic state to the elastic, becomes strong enough to withstand the metallostatic pressure² moving away from the mold as a result of the shrinking process. For (KIM, 2003), another factor of secondary importance would be the expansion of the metal mould that is initially at a temperature below that of the liquid.

The work presented in (VYNNYCKY, 2009), although developed for continuous casting, reviews three methodologies adopted for the study of the influence of the air layer analogous to those that can be used for conventional casting: in the first, a heat transfer coefficient is assumed for the calculation of the temperature field which, in turn, is used to calculate the displacement of the solid front in relation to the mould. The temperature field is not corrected (SCHWERDTFEGGER; SATO; TACKE, 1998); in the second approach, experiments are conducted to calculate the heat transfer coefficient in relation to the thickness of the air layer and the value obtained is used to calculate the temperature field (TROVANT; ARGYROPOULOS, 1998); in the third approach, there is a coupled model in which the boundary conditions for the temperature problem

² Metallostatic pressure is the pressure caused by the metal, just as the hydrostatic pressure is caused by water. (RESUMO..., 2013)

contain terms that depend on the displacement of the solid front in relation to the mould and vice versa (GRILL; SORIMACHI; BRIMACOMBE, 1976), (SUN *et al.*, 2007).

In (PATIL *et al.*, 2015), the air layer is considered in a thermal resistance scheme built to specify the temperature boundary conditions. Between the ingot mould and the environment, the author considers the following boundary condition:

$$-k \frac{\partial T}{\partial \mathbf{n}} = h(T - T_{\text{ext}}), \quad (2.29)$$

where h is the heat transfer coefficient, $\mathbf{n}$ is the normal vector perpendicular to the surface and T_{ext} is the external temperature. The above formula can incorporate both the convection and radiation effect, where h is given by:

$$h = h_{\text{cv}} + \varepsilon_r \sigma_r (T + T_{\text{ext}})(T^2 + T_{\text{ext}}^2), \quad (2.30)$$

h_{cv} being the convection heat transfer coefficient, ε_r the emissivity of the body and σ_r the Stefan Boltzmann constant. The second term on the right-hand side of the equation refers to the exchange of heat for radiation in which the emissivity varying in the range $0 \leq \varepsilon_r \leq 1$ indicates how efficient a surface is to emit radiation, compared to an ideal emitter (a black-body of the same temperature) (INCROPERA; DEWITT, 1985).

On the ingot surface that is in contact with the mould, the Robin boundary condition is imposed based on Fourier's law of heat conduction across two materials:

$$-k \frac{\partial T}{\partial \mathbf{n}} = \frac{1}{R_{\text{eq}}}(T - T_{\text{mould}}), \quad (2.31)$$

where T_{mould} is the temperature at the mould interface, and R_{eq} is the thermal resistance to the transfer between the two domains in which the resistance provided by the layer of air, and the local normal stress as follows:

$$R_{\text{eq}} = \begin{cases} \frac{1}{\min\left(\frac{1}{R_0}, \frac{1}{R_{\text{air}}}, \frac{1}{R_{\text{rad}}}\right)} + R_s, & \text{if } e_{\text{air}} > 0, \\ \frac{1}{1/R_0 + 1/R_{\text{rad}}} + R_s, & \text{if } e_{\text{air}} = 0. \end{cases} \quad (2.32)$$

$$R_{\text{air}} = \frac{e_{\text{air}}}{\kappa_{\text{air}}} \quad R_s = \frac{e_s}{k_s}, \quad (2.33)$$

where e_{air} and e_s are the thickness of the air layer and the slag³, respectively and κ_{air} and k_s represent their thermal conductivities. R_0 is the nominal resistance that depends on the surface roughness, and R_{rad} is the resistance associated with radiation heat transfer:

$$R_{\text{rad}} = \frac{1/\varepsilon + 1/\varepsilon_{\text{mould}} - 1}{\sigma_r(T^2 + T_{\text{mould}}^2)(T + T_{\text{mould}})}, \quad (2.34)$$

³ The slag (*slag*) is a by-product obtained in the separation of an ore, usually formed by a mixture of metal oxides and silicon dioxide. In the reduction process, the iron liquefies and is called pig iron or first melting iron. In this case, impurities such as limestone, silica etc. they form slag, which is the raw material for the manufacture of cement. (IAB, 2017)

Such expressions basically describe the heat exchange between the liquid and the environment, through the walls of the mould.

The boundary conditions applied for the solute is usually zero flow for the domain boundaries, that is, there is no solute transport through the walls:

$$\frac{\partial c}{\partial \mathbf{n}} = 0, \quad (2.35)$$

where $\mathbf{n}$ is the outward normal.

2.3 Multi-domains modelling

The approach that considers mass, momentum and energy conservation separately for each of the regions and coupled across the moving boundaries have been shown to be more efficient when dealing with the interaction between the liquid and solid phases (PICKERING, 2013). An important drawback of the multi-domain approach, however, is that it requires the tracking of the boundaries between solid, mushy zone and liquid region. This is often a difficult task, particularly as the boundaries can take complex morphologies, in fact, for many years authors have constantly tried to avoid it.

2.3.1 Flemings and co-workers

The work of Fujii and Flemings (FUJII; POIRIER; FLEMINGS, 1979) was the first attempt on developing a model for the macrosegregation study that would couple heat and momentum transport equations and solve them simultaneously. Before that, in the series of work also developed in collaboration with Flemings (FLEMINGS; NEREO, 1967; FLEMINGS; NEREO, 1968a; FLEMINGS; NEREO, 1968b; MEHRABIAN; KEANE; FLEMINGS, 1970; KOU; POIRIER; FLEMINGS, 1978), the temperature profile in the mush region had either been assumed or measured to serve as input to the convection field in the interdendritic liquid.

In their work, a multi-component alloy is considered and the progression of the solidus and liquidus isotherms are specified as functions of time based on the experimental works developed by a third part, i.e. the movement of the interfaces are an input to the model. The liquidus and solidus isotherm velocities, namely U_{liq} and U_{sol} , are used to calculate the velocity at the position, S_x , as

$$S_x = \frac{x}{x_m}(U_{liq} - U_{sol}) + U_{sol}, \quad (2.36)$$

for the material at the location x , considering the mushy zone thickness x_m . The velocity S_x is, in turn, used to estimate the time rate of change of the liquid fraction χ as

$$\frac{d\chi}{dt} = S_x \frac{\partial \chi}{\partial x} + \frac{\partial \chi}{\partial t}, \quad (2.37)$$

and, analogously, for the temperature T

$$\frac{dT}{dt} = S_x \frac{\partial T}{\partial x} + \frac{\partial T}{\partial t}. \quad (2.38)$$

The fluid flow in the mushy zone is modelled using the Darcy's Law, while the local solute redistribution equation relates the local compositional changes to the temperature change and interdendritic flow velocity, while the energy equation relates the local temperature change to thermal properties and interdendritic flow velocity. Following the methodology presented in the article, after solving those equations at the time t_n , it is possible to compute $\partial \chi / \partial t$ and $\partial T / \partial t$ in eq. (2.37–2.38) and apply both relations to determine χ and T at t_{n+1} using a simple forward difference method.

2.3.2 Szekely and Jassal (SZEKELY; JASSAL, 1978)

Published around the same time, the work of Szekely and Jassal (SZEKELY; JASSAL, 1978), proposes a model with three set of equations, where the differential energy balance is defined for each region and the laminar Navier-Stokes equations are defined for the mush and liquid regions. The authors were interested in studying the evolution of the convective field and compared the numerical results against experimentally measured values considering a two-dimensional domain $([0, W] \times [0, L])$ filled with a binary solution, where surfaces corresponding to $y = 0$ and $y = L$ are insulated, and the side walls are subjected to the boundary conditions

$$T(0, y) = T_c, \quad (2.39)$$

$$T(W, y) = T_w, \quad (2.40)$$

where T_c is below solidus temperature, and T_w is above liquidus temperature, i.e. the domain is cooled from one side and heated up from the other.

The segregation effects can not be studied in this model, as the solute redistribution equations are not included in the formulation. Moreover, the characteristic moving-boundary type boundary conditions were also absent, as the position of the liquidus and solidus lines $X_{liq}(t)$, $X_{sol}(t)$ are implicitly defined by

$$T = T_{liq}, \quad \text{at} \quad x = X_{liq}(t), \quad (2.41)$$

$$T = T_{sol}, \quad \text{at} \quad x = X_{sol}(t) \quad (2.42)$$

for the liquidus and solidus temperatures T_{liq} , T_{sol} . The authors also consider that the liquid fraction can be calculated from an algebraic relation

$$\chi = \frac{k_p}{1 - k_p} \left(\frac{1}{k_p} - \frac{mc_0}{T - T_0} \right), \quad (2.43)$$

where k_p is a partition ratio, m is the liquidus line slope, c_0 is the initial concentration and T_0 is the melting point for the pure material, having the obtained temperature profile as an input.

2.3.3 Voller (VOLLER, 1997)

In one of the earliest approaches, as presented by Voller in his series of works (VOLLER; BRENT; PRAKASH, 1989; VOLLER; SUNDARRAJ, 1995; VOLLER, 1997; VOLLER, 1998), the movement of those interfaces is modelled into a one-dimensional problem using Stefan condition, which states the rate of change in latent heat as equivalent to the amount by which the conductive heat flux jumps across the interface.

Particularly in (VOLLER, 1997), the problem is formulated for a semi-infinite melt $[0, Y_{mould}]$ being cooled by a boundary that is held at a constant temperature T_w below solidus temperature T_{sol} , valid for the case when the solidification is of eutectic nature $T_{sol} = T_{eut}$ and

the initial temperature of the melt is just above the liquidus temperature of the alloy, i.e. low superheat, so that heat transfer in the full liquid region can be adequately modeled by heat conduction. With the adequate interpretation and simplifications of the phase diagram the model may be applied to multi-component alloys, e.g. ternary alloys.

The equations for the three regions are defined as follows

- Solid region ($0 \leq y \leq Y_{\text{eut}}$)

The governing equation for temperature T is

$$\frac{\partial T}{\partial t} = R\alpha \frac{\partial^2 T}{\partial y^2}, \quad (2.44)$$

where α is the thermal diffusivity, and the ratio R between the solid and the liquid density is given by

$$R = \rho_s / \rho_l. \quad (2.45)$$

- Mush region ($Y_{\text{eut}} \leq y \leq Y_{\text{liq}}$)

The governing equation for temperature is

$$[(\chi + (1 - \chi)R)] \frac{\partial T}{\partial t} + U \frac{\partial T}{\partial y} = k \frac{\partial^2 T}{\partial y^2} - R \frac{\Delta H_f}{c} \frac{\partial \chi}{\partial t}, \quad (2.46)$$

where χ is the liquid fraction, U is the volume flux of interdendritic liquid, ΔH_f is the latent heat and c is the specific heat.

The solute concentration is modelled using

$$[\chi + \beta k_p R (1 - \chi)] \frac{\partial C_1}{\partial t} + U \frac{\partial C_1}{\partial y} = (k_p - 1) R C_1 \frac{\partial \chi}{\partial t}, \quad (2.47)$$

where k_p is the partition ratio and C_1 is the concentration of solute in the liquid phase. The parameter β allows for a flexible modelling of the microsegregation using either the Scheil equation, the lever rule, or an interpolation between the two, as it will be discussed in Section 5.1.2.

The mass balance is governed by

$$\frac{\partial U}{\partial y} = (1 - R) \frac{\partial \chi}{\partial t}. \quad (2.48)$$

- Liquid region, ($Y_{\text{liq}} \leq y, y = Y_{\text{mould}}$ is the far field condition $y \rightarrow \infty$)

The governing equation for temperature, analogously to the form admitted in eq. (2.44), is

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial y^2}. \quad (2.49)$$

- Boundary conditions

At $y = 0$, the melt is cooled by the fixed temperature T_w

$$T = T_w < T_{\text{eut}}. \quad (2.50)$$

On the moving boundary $y = Y_{\text{eut}}$, the temperature and the discontinuities across the eutectic front are represented by

$$T = T_{\text{eut}}, \quad (2.51)$$

$$\alpha \left[\frac{\partial T}{\partial y} \right] = -R\chi \frac{\Delta H_f}{c} \frac{dY_{\text{eut}}}{dt}, \quad (2.52)$$

$$[U] = (1 - R)\chi \frac{dY_{\text{eut}}}{dt}. \quad (2.53)$$

On the moving boundary $y = Y_{\text{liq}}$, the temperature and the liquid fraction are defined using

$$T = T_{\text{liq}}, \quad (2.54)$$

$$\left[\frac{\partial T}{\partial y} \right] = 0, \quad (2.55)$$

$$\chi = 1. \quad (2.56)$$

using the liquidus temperature T_{liq} , while at the boundary as $y \rightarrow \infty$ the temperature is set by

$$T = T_{\text{liq}} + \delta T, \quad (2.57)$$

where δT is the superheat.

A similarity solution is then obtained for the model described by eq. (2.44–2.57) with complete coupling of solute and temperature fields in the mushy region. In this solution, a similarity variable is

$$\eta = \frac{y}{2(\alpha t)^{1/2}}, \quad (2.58)$$

and the movement of the solid-mush, mush-liquid interfaces are assumed to follow the relationships

$$Y_{\text{eut}} = 2\eta_{\text{eut}}(\alpha t)^{1/2}, \quad (2.59)$$

$$Y_{\text{liq}} = 2\eta_{\text{liq}}(\alpha t)^{1/2} \quad (2.60)$$

such that in the η -space the interfaces are fixed at the positions η_{eut} and η_{liq} , i.e. the solid region is defined in $0 \leq \eta \leq \eta_{\text{eut}}$, the mush region in $\eta_{\text{eut}} \leq \eta \leq \eta_{\text{liq}}$, and the liquid region occupies the semi-infinite interval $\eta \geq \eta_{\text{liq}}$.

Using the similarity transformation, the solution for heat equations in the solid eq. (2.44) and liquid regions eq. (2.49), can be found analytically, while the variables T , χ , U , η_{eut} , η_{liq} in the mush regions are obtained numerically.

Figure 2.4 – Single-phase Stefan problem. (a) domain configuration, (b) position of liquid-solid interface. Adapted from (CRANK, 1987).

2.4 Stefan problem

Stefan problems are usually the term used to denote a category of moving-boundary problems, as a reference to the work of J. Stefan published in the late 19th century consisting of a series of reports (STEFAN, 1889b; STEFAN, 1889a; STEFAN, 1891) originally devoted to the study of the melting polar ice cap. A systematic presentation of the mathematical developments, including the uniqueness of a classical solution, extension to two or three dimensional domain and other surveys can be found in classic books (RUBINŠTEIN, 2000; CARSLAW; JAEGER, 1959; ALEXIADES, 1992).

According to (CRANK, 1987), the simplest version of the problem is the melting of a semi-infinite sheet of ice, initially at the melting temperature $T = T_m$, being melted from the boundary with constant temperature $T = T_L$, as shown in Fig. 2.4.a. As the domain occupied by water in liquid phase starts to grow, an interface between the liquid and the solid regions moves from the surface into the sheet bulk. The interface trajectory is denoted by $S(t)$ as in Fig. 2.4.b, where t denotes the time-variable, and Y is the spatial coordinate.

Thus, the problem consists on finding a temperature profile in the liquid region $T(Y, t)$ and the position of the interface $S(t)$ that satisfy the heat flux model:

- Governing equation

$$c_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial Y^2}, \quad 0 < Y < S(t), \quad t > 0, \quad (2.61)$$

where c_p is the specific heat, ρ is the material density, k is the heat conductivity, all of which are assumed to be constants.

- Boundary condition

$$T(0, t) = T_L, \quad T_L > T_m, \quad t > 0, \quad (2.62)$$

clearly another boundary condition is needed to solve the second-order eq. (2.61), such condition is given by

$$T(S(t), t) = T_m, \quad t > 0 \quad (2.63)$$

- Initial conditions

$$T(Y, 0) = T_m, \quad Y > 0, \quad (2.64)$$

$$S(0) = 0, \quad (2.65)$$

a further condition is still necessary to uniquely determine the solution to the problem, which will be supplied by the so-called Stefan condition,

$$-k \frac{\partial T}{\partial Y} = \rho \Delta H_f \frac{dS}{dt}, \quad Y = S(t), \quad t > 0, \quad (2.66)$$

where ΔH_f is the latent heat. It is noticeable that the initial condition leads to a problem where the temperature profile across the solid region is a constant T_m , thus only one phase is “active”. This represents an important restriction since a limited number of phase-change processes lead to a single-phase situation, e.g., the solidification of pure materials, in contrast to alloys involving two or more elements. On a different problem involving a solid region in which the initial temperature T_{ini} is below the melting point, i.e., $T_{ini} < T_m$, the heat flux must be considered in both regions, and we get the configuration known as the two-phase Stefan problem posed on a finite domain with length L :

- Governing equations

For the solid region $0 < Y < S(t)$,

$$c_{ps} \rho_s \frac{\partial T_s}{\partial t} = k_s \frac{\partial^2 T_s}{\partial Y^2}, \quad t > 0, \quad (2.67)$$

for the liquid region $S(t) < Y < L$,

$$c_{pl} \rho_l \frac{\partial T_l}{\partial t} = k_l \frac{\partial^2 T_l}{\partial Y^2}, \quad t > 0, \quad (2.68)$$

where the material properties are constant across each domain and the subscripts s and l denote, respectively, the variables at the solid, or liquid regions.

- Boundary conditions

$$T_s(0, t) = T_L, \quad T_L > 0 \quad t > 0,$$

$$T_s(S(t), t) = T_l(S(t), t) = 0, \quad t > 0$$

- Initial conditions

$$T_s(Y, 0) = T_{ini}, \quad T_{ini} > T_m \quad Y > 0,$$

$$S(0) = 0.$$

The Stefan condition can be derived by looking at Fig. 2.5, where the moving boundary moves by dS during a time interval dt . The amount of heat that enters the solid region is $-k_s dt \partial T_s / \partial Y$, while the amount $-k_l dt \partial T_l / \partial Y$ leaves the liquid region towards the shaded element, whose area represents the amount of heat necessary to melt the solid material that previously occupied that region in a relation that is proportional to the latent heat $\rho \Delta H_f dS$. Then, the heat balance leads to:

$$\left[k \frac{\partial T}{\partial Y} \right]_{-}^{+} = k_l \frac{\partial T_l}{\partial Y} - k_s \frac{\partial T_s}{\partial Y} = \rho \Delta H_f \frac{dS}{dt}, \quad (2.69)$$

which can be interpreted as the heat flux jump at the interface $S(t)$ that moves until the final length L is reached at the time $t = t_f$, according to Fig. 2.4.b, when no density difference is taken into account.

Figure 2.5 – Space-time diagram for the two-phases Stefan problem

Usually the exact solutions take the form of functions of the single variable $Y/t^{1/2}$, known as similarity solutions, this methodology including some explanatory examples is briefed in Section 2.5. Over the last century, the original Stefan problem has been extended in order to be applied to solidification of alloy systems, among other applications (ALEXIADES, 1992).

2.5 Similarity solutions

In the process of solving a mathematical model that describes a certain physical phenomena, one of the possible approaches is to reduce the resulting system of partial differential equations to a system of ordinary differential equations using some broadly studied techniques, one of which is the so called similarity transformation. This approach consists in defining a similarity variable as the independent variable of the ODE system by combining the space and time variables. According to (SACHDEV; JANNA, 2001), this procedure was, in its early days,

employed as a mean to obtain a set of ODEs that could be solved by hand calculators due the lack of computational resources, as did Taylor in the 50's when investigating the propagation of shock waves and the mechanical effects expected from intense explosions (TAYLOR, 1950). Nowadays the search for exact solutions can provide a better understanding of the mathematical structure of the solutions and a deeper comprehension of the physical problem described by the mathematical model.

The approach was applied to find an analytical solution on solidification problems, firstly as the Rubinstein solution for planar front alloy solidification (RUBINŠTEIN, 2000), the solution of a mushy phase change with an imposed linear liquid fraction profile (GOODMAN, 1967), and the Neumann solution of the Stefan problem (CRANK, 1987), which is constructed below for the problem presented in Section 2.4, consisting on eq. (2.61) subjected to conditions of eqs. (2.62–2.66).

The similarity variable is introduced

$$\xi = \frac{Y}{t^{1/2}}, \quad (2.70)$$

the temperature function is in the form

$$F(\xi) = T(Y, t), \quad (2.71)$$

where the position of the solid-liquid interface $S(t)$ is sought, assuming that it is proportional to $t^{1/2}$ by a constant A :

$$S(t) = At^{1/2}. \quad (2.72)$$

Changing the variables and substituting into eq. (2.61) using

$$\frac{\partial \xi}{\partial t} = -\frac{1}{2}Yt^{-3/2}, \quad \frac{\partial \xi}{\partial Y} = t^{-1/2},$$

leads to

$$\xi \frac{\partial F}{\partial \xi} = -\frac{1}{\alpha} \frac{\partial^2 F}{\partial \xi^2}, \quad (2.73)$$

where $\alpha = k/(\rho c_p)$. Now, integrating eq. (2.73) we obtain

$$F(\xi) = C_1(\pi\alpha)^{1/2} \operatorname{erf}\left(\frac{\xi}{2\alpha^{1/2}}\right) + C_2. \quad (2.74)$$

The boundary condition 2.62 implies that

$$C_2 = T_L, \quad (2.75)$$

while the constant C_1 is calculated from eq. (2.63)

$$C_1 = -\frac{T_m - T_L}{(\pi\alpha)^{1/2} \operatorname{erf}(A/2\alpha^{1/2})}. \quad (2.76)$$

To solve for the position of the solid-liquid interface, one can use

$$\lambda = \frac{A}{2\alpha^{1/2}}, \quad \Delta T = T_L - T_m, \quad St = \frac{c_p \Delta T}{\Delta H_f}, \quad (2.77)$$

where St is the dimensionless Stefan number. Taking the derivative of $F(\xi)$ from 2.74,

$$\frac{\partial F}{\partial \xi} = C_1 e^{-\xi^2/4\alpha}, \quad (2.78)$$

replacing it into the Stefan condition from eq. (2.66), and recalling the assumption for $S(t)$ on eq. (2.72) leads to

$$\xi = A, \quad \text{at} \quad Y = S(t), \quad (2.79)$$

$$e^{\lambda^2} \alpha^{1/2} \frac{A}{2} \text{erf}(\lambda) = \frac{k}{\rho \Delta H_f} \frac{\Delta T}{\pi^{1/2}}, \quad (2.80)$$

multiplying by α^{-1} ,

$$\lambda e^{\lambda^2} \text{erf}(\lambda) = \frac{St}{\pi^{1/2}}. \quad (2.81)$$

Now one can write $S(t)$ and $T(Y, t)$ in terms of λ , as

$$T(Y, t) = T_L - \Delta T \frac{\text{erf}\left(\frac{Y}{2(\alpha t)^{1/2}}\right)}{\text{erf}(\lambda)}, \quad (2.82)$$

$$S(t) = 2\lambda(\alpha t)^{1/2}, \quad (2.83)$$

where λ is the root of the transcendental equation (2.81). Once the root is found, the solution of the Stefan problem is given by eqs. (2.82) and (2.83).

Applied to the study of unidirectional solidification of binary alloys, the similarity transformation has been used with different level of simplifications, including: assumption of aqueous solution sometimes excluding the solid region and neglecting macrosegregation (BRAGA; VISKANTA, 1990); or considering three regions model, but still neglecting the macrosegregation caused by the fluid flow (FANG *et al.*, 1984; WORSTER, 1986); or accounting for the macrosegregation but not including the solid region (CHIARELI; WORSTER, 1992).

A comprehensive work on the field has been developed by Voller, where a solution is obtained through similarity transformation on a three regions model considering the macrosegregation, and fluid flow, along with eutectic reaction and non-aqueous solution (VOLLER, 1997).

As an effort to make the mathematical model more reliable and accurate when compared to the physical phenomena that it attempts to describe, it is desirable to reduce the simplifying hypothesis in an endeavor that usually leads to a highly complex model. In the process, the problem may lose some of its symmetries and the group of transformations to which the model

is invariant may be depleted, making the self-similar form become very restricted or even cease to exist. In general, a numerical solution of the ordinary differential equation is required, which will rely again on numerical methods and elevated computing capabilities, but can be as accurate and less demanding than solving the original governing PDE system.

2.6 Arbitrary Lagrangian-Eulerian method

In the task of solving a model involving solid, mush and liquid regions, with the three being separated by moving solid-mush and mush-liquid interfaces, the Arbitrary Lagrangian-Eulerian method may be used as an effort to provide a clear delineation of the interfaces combining two classical descriptions of motion: the Lagrangian description and the Eulerian description (DONEA *et al.*, 2004).

Arbitrary Lagrangian-Eulerian methods were first introduced by C.W. Hirt and his coworkers from *Los Alamos Scientific Laboratory* in the 70's (HIRT; AMSDEN; COOK, 1974), as a numerical technique for the solution of Navier-Stokes equation, using a finite difference mesh with vertices that may move with the fluid, following the Lagrangian Coordinate System, be held fixed, as the Eulerian Coordinate System, or move in any other prescribed way. That flexibility allows to retain the advantages of both frameworks, optimizing accuracy, robustness, and computational efficiency (MAIRE *et al.*, 2008). This section briefly describes the method and its application, while an insight into the ALE finite element formulation is given by observing the developments in (HUGHES; LIU; ZIMMERMANN, 1981).

A first and perhaps more natural way to observe the fluid flow, begins by thinking of it as the transport of material from one position to the next, thus it involves tracking the specific and identifiable volumes that are carried around as well as their trajectories. As the nodes are attached to the moving material, variation of state variables such as temperature, velocity, concentrations, throughout the process can be more easily predicted. For large deformation problems, deformation of the mesh with the material lead to mesh distortion. In structural mechanics and other fields of physics dealing with a possibly anisotropic, solid material are most conveniently simulated using Lagrangian formulation.

A second way basically consists on observing the fluid velocity at locations that are fixed in space. As the control volume is fixed, the flow of material through the volume is analyzed, and there is no problem related to mesh distortion. Another advantage is the shorter computational time when compared to the Lagrangian approach. In contrast to the Lagrangian formulation, the Eulerian is usually more convenient when the focus is on simulating the physical state at fixed points in space, particularly when liquids and gases are involved. However, using the Eulerian formulation brings an inherent problem when handling the moving domain boundaries, that is because the set of spatial points inside the domain boundaries will change with time, while the physical quantities are referred to a fixed point in space. To overcome this challenge and allow

moving boundaries, the Eulerian equations must be transformed in order to describe the physical quantities as functions of some coordinate system in which the domain boundaries are fixed, with one-to-one map from the current spatial domain configuration. Rewriting the governing equations in this way, on a freely moving mesh, results in an arbitrary Lagrangian-Eulerian (ALE) method.

The Lagrangian, Eulerian and the ALE reference domains are summarized in Fig. 2.6 together with the transformations between its coordinate systems. The material domain $\Omega_Z \subset \mathbb{R}^d$ corresponds to the original domain configuration, with d denoting the number of spatial dimensions. Defining the open time interval $(0, T) \subset \mathbb{R}$, the motion of material domain is given by the mapping $\psi : \Omega_Z \times (0, T) \rightarrow \mathbb{R}^d$, where the image of the Lagrangian description Ω_Z at time t is the spatial domain Ω_Y on the Eulerian description, and the image of $Z \in \Omega_Z$ is denoted by

$$Y : Y = \psi(Z, t). \quad (2.84)$$

Figure 2.6 – Notations of domains and mappings for the ALE description of motion.

The reference domain $\Omega_X \subset \mathbb{R}^d$ is held fixed for all the time interval and the mapping to the spatial domain is given by $\Phi : \Omega_X \times (0, T) \rightarrow \mathbb{R}^d$, where Ω_Y is the image of Ω_X at time t , and the image of $X \in \Omega_X$ is denoted by

$$Y : Y = \Phi(X, t). \quad (2.85)$$

We can think of the spatial domain Ω_Y as the domain where the fluid mechanics problem takes place, while the material domain Ω_Z corresponds to the domain occupied at the initial time $t = 0$ by the material particles that occupy Ω_Y at time t and Ω_X is used as reference for motion description and spatial discretization. Thus, Ω_X is always fixed while Ω_Y and Ω_Z may vary with time. A third mapping from the reference domain to the spatial domain is defined by $\phi = \Phi^{-1} \circ \psi$, assuming that ψ and Φ are smooth functions.

The mapping function ψ between the material and spatial domain represents the particle motion, while the mapping Φ from the reference to the spatial domain is the mesh motion, and the motion of the material observed by the reference frame is given by the mapping ϕ . If we set $\Omega_X = \Omega_Z$, we obtain the Lagrangian description, while the Eulerian description is obtained by setting $\Omega_X = \Omega_Y$.

The ALE can be used in a variety of problems involving the casting and processing of metal alloys, such as the punch forging and plane strain metal extrusion processes (GADALA; WANG, 1998), two-dimensional metal cutting problems (OLOVSSON; NILSSON; SIMONSSON, 1999), mould filling simulations - where the main issue is the tracking of the free surface separating the fluid domain from the rest of the mould cavity, or tracking the interfaces between solid and liquid regions during progressive solidification of a cast part (BELLET; FACHINOTTI, 2004).

When deforming the domain using a moving mesh feature it may be advised to incorporate smoothing techniques in order to propagate the moving boundary displacement throughout the domain, to obtain a smooth mesh deformation everywhere. This is done by solving partial differential equations for the mesh displacement with the boundary conditions given by the movement of the boundaries.

For the Laplace smoothing, the deformed mesh with positions x and y as degrees of freedom are introduced in the model, solving the equation

$$\frac{\partial^2 x}{\partial X^2} + \frac{\partial^2 x}{\partial Y^2} = 0, \quad (2.86)$$

$$\frac{\partial^2 y}{\partial X^2} + \frac{\partial^2 y}{\partial Y^2} = 0. \quad (2.87)$$

For the Winslow smoothing, the equation is solved as

$$\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} = 0, \quad (2.88)$$

$$\frac{\partial^2 Y}{\partial x^2} + \frac{\partial^2 Y}{\partial y^2} = 0, \quad (2.89)$$

where the spatial domain coordinates are (x, y) and (X, Y) corresponds to the material domain coordinates. The coordinates X and Y satisfy the Laplace equations as functions of the x and y coordinates.

As one can observe from the equations above, the Laplace smoothing is linear and uses a single uncoupled equation for each coordinate direction. It is in fact the cheapest option in terms of use of computational resources, however it does not incorporate any mechanism that prevents the inversion of deformed elements. Thus, the method is only suited for small deformations around the initial shape.

The Winslow smoothing method, on the other hand, is nonlinear and has a system of equations for all coordinate directions, which makes it more expensive to solve. However, it has a theoretical property that assures that continuous solutions to the equations always have positive volume everywhere. Many comparisons between these two methods have been performed based on quality measures, shape factor and minimum angle and there is a widely held consensus that the Winslow method is the smoother of choice ([KNUPP, 1999](#); [FALSAFIOON *et al.*, 2014](#)). More advanced methods have been developed such as Yeoh smoothing method, which may generally produce best results when looking at the mesh quality, but its strong non-linearity may lead to convergence problems, specially for models that are already fairly complex ([COMSOL, 2018](#)).

PIPE FORMATION MODELLING

As the shrinkage cavity may cause severe changes in the ingot final dimensions, it represents an indispensable feature to any two-dimensional code that attempts to solve the solidification problem in metal ingots. To the extent of this work, it takes into account only the ingot geometry, the heat dissipation and the heat exchange with the surroundings, while assuming a homogeneous solute concentration throughout the domain.

The mechanism that lead to the formation of the cavity, as described in Section 1.1, can be traced back to the inherent changes in density as the material solidifies. Depending on the material properties and boundary conditions affecting the mould, the cavity may grow deep into the ingot, see Fig. 3.1. According to (FREDRIKSSON; ÅKERLIND, 2006), in order to reduce the final height of this cavity, one can employ the technique called hot-top, which consists of installing thermal insulators in the upper part of the mould. The apparatus causes the upper part of the ingot to be the last region to solidify, thus acting as a reservoir of melt being fed into the rest of the ingot as its volume decreases, minimizing the final height of the pipe.

Figure 3.1 – Solidification and formation of central cavity.

3.1 Mathematical formulation

From the point of view of mathematical modeling, this phenomenon leads to the modification of the original domain. Therefore, for the correct resolution of the macrosegregation problem, the objective is to include the contraction process in order to keep the computational domain comparable to the final shape of the ingot.

At first, the case of solidification and contraction of a pure metal will be taken into account, having a melting temperature of T_{sol} . From Figure 3.2, the mass conservation can be established:

$$\frac{1}{2}\rho_l A_i = \rho_s A_s + \rho_l A_{ns}, \quad (3.1)$$

where A_i is the initial liquid area ($A_i = HW$), A_s is the solid pore area and A_{ns} is the pore area filled with liquid or metal in mush form, which can be expressed by integrals leading to:

$$\rho_l A_i = \rho_s \int_0^W s(x', t) dx' + \rho_l \left(x^*(t) h(t) - \int_0^{x^*(t)} s(x', t) dx' \right), \quad (3.2)$$

where

$$h(t) = s(x^*(t), t), \quad (3.3)$$

Differentiating equation 3.2 for t , using the Leibniz' rule, we get

$$\rho_s \int_0^W \frac{\partial s}{\partial t}(x', t) dx' + \rho_l \left(x^*(t) \dot{h}(t) - \int_0^{x^*(t)} \frac{\partial s}{\partial t}(x', t) dx' \right) = 0, \quad (3.4)$$

Figure 3.2 – Shrinkage cavity sketch under Dirichlet boundary condition.

The Dirichlet condition can be applied at the border to determine the temperature on the walls, in the form: $T = T_{\text{wall}}$, where $T_{\text{wall}} < T_{\text{sol}}$. Thus solidification would begin immediately along the entire wall of the mould. Soon the contraction cavity would be formed from $y = H$, as shown in Figure 3.2. In addition, if the boundaries $y = 0$ and $y = H$ are both insulated, then it is possible to apply the solution by similarity as in (VYNNYCKY, 2012). In this case:

$$x^*(t) \approx \frac{W}{2} - \lambda t^{1/2}, \quad s \approx H \quad (3.5)$$

where λ is a constant to be determined. For small t values you can assume:

$$\frac{1}{2}\rho_l HW \approx \rho_s H \lambda t^{1/2} + \rho_l \left(\frac{W}{2} - \lambda t^{1/2} \right) h(t), \quad (3.6)$$

which is consistent when $t \rightarrow 0$, since $h \rightarrow W$. For cases like this, in (VYNNYCKY; KIMURA, 2007) and (VYNNYCKY; KIMURA, 2015) the ALE method (*Arbitrary Lagrangian Eulerian Method*) was used using $\rho_s = \rho_l$. The similarity solution already mentioned in (VYNNYCKY, 2012) is developed for $\rho_s \neq \rho_l$.

Figure 3.3 – Pipe formation scheme under Neumann boundary conditions.

If Neumann or Robin conditions are imposed, then solidification must start at the corners of the lower boundary and move upwards, which indicates that the deformation cavity will not be formed from a distance $y = H$, as shown in Figure 3.3. For this case, however, the ALE method suggested above cannot be applied, and the initial similarity solution is not appropriate. If the boundaries at $y = 0$ and $y = H$ are both insulated, and $\rho_s = \rho_l$, it was demonstrated in (MITCHELL; VYNNYCKY, 2014) that:

$$s(t) \sim \frac{W}{2} - \mu(t - t_{\text{sol}})^{3/2}, \quad (3.7)$$

where μ is a constant calculated in the reference. In another approach, instead of trying to trace the solidification frontier by using eq. 3.5 or eq. 3.7, one can use the energy conservation and latent heat equation as a source term. In this case, one can denote the liquid fraction by χ , in the following formulation:

$$\rho \left(c_p + \Delta H_f \frac{d\chi}{dT} \right) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right), \quad (3.8)$$

where:

$$\rho = \rho_l \chi + \rho_s (1 - \chi), \quad (3.9)$$

$$c_p = c_{pl} \chi + c_{ps} (1 - \chi), \quad (3.10)$$

$$k = k_l \chi + k_s (1 - \chi), \quad (3.11)$$

where ΔH_f represents the latent heat of the fusion. And the fraction can be written, as in (LAGERSTEDT, 2004):

$$\chi = \begin{cases} 0, & T \leq T_{sol} \\ 1 - \frac{T_{liq} - T + \frac{2}{\pi} (T_{sol} - T_{liq}) \left(1 - \cos \left(\frac{\pi}{2} \left(\frac{T - T_{liq}}{T_{sol} - T_{liq}} \right) \right) \right)}{(T_{liq} - T_{sol}) \left(1 - \frac{2}{\pi} \right)}, & T_{sol} < T < T_{liq} \\ 1, & T \geq T_{liq} \end{cases}$$

therefore:

$$\frac{d\chi}{dT} = \begin{cases} 0, & T \leq T_{sol} \\ \frac{1 - \sin \left(\frac{\pi}{2} \left(\frac{T - T_{liq}}{T_{sol} - T_{liq}} \right) \right)}{(T_{liq} - T_{sol}) \left(1 - \frac{2}{\pi} \right)}, & T_{sol} < T < T_{liq} \\ 0, & T \geq T_{liq} \end{cases}$$

The boundary condition on the walls can be imposed as:

$$k \frac{\partial T}{\partial n} = h(T - T_0), \quad (3.12)$$

where T_0 represents the environment temperature, k is the thermal conductivity, and h indicates the heat transfer coefficient. At this point it is possible to include another phenomenon characteristic of the solidification process in ingots: the formation of an air layer between the ingot and the mould wall acting as an insulator and making it difficult to lose heat through the walls. As described in (LAGERSTEDT, 2004), before the formation of the air gap, the heat transfer occurs primarily by conduction, so that it forms, however, the coefficient must be reduced and possibly take into account the transfer by irradiation. It is also noted, according to the author, that the layer is of such thickness that the heat exchange by convection within that layer can be disregarded.

3.2 Numerical Implementation

The Finite Elements software Comsol Mutiphysics software was used to solve the temperature eq. (3.8) subject to eq. (3.11–3.12), combined with the *deformed geometry* interface - capable of imposing deformations at specific points in the mesh. Such deformations were calculated using a MatLab script that reads the temperature calculated in each region of the domain for a given time step t^n and eq. (3.2). The obtained domain deformation is communicated back to Comsol, in order to compute the temperature distribution at the new time t^{n+1} . The time discretization is carried out using a second-order backwards differentiation formula (BDF).

3.3 Numerical Results

Computational tests were carried out to approximate the final shape of the steel ingot taking into account the shrinkage cavity produced during the solidification process.

The studied equations are defined in the relation 3.8 and subsequent expressions. The domains used are based on the schemes shown in Figure 3.4, where the ingots has approximately 4.2 tonnes. The computational domain involves half of the two-dimensional section as shown in Figure 3.5.(c).

Figure 3.4 – Geometry of steel ingot. Measures in mm.

For Neumann's boundary condition, the heat flow to the mould walls is defined as

Figure 3.5 – Mould sketch based on original mould dimensions.

described in equation 3.12, where

$$h = \begin{cases} 1000 \text{ Wm}^{-2}\text{K}^{-1}, & t \leq 300s \\ 170 \text{ Wm}^{-2}\text{K}^{-1}, & t > 300s \end{cases}$$

here the the air gap between the mould and the metal in the process of solidification is taken into account and effectively lowering the heat exchange rate after 300 seconds.

Parameter	Value	Unit	Description
c_{pl}	620	$\text{J kg}^{-1}\text{K}^{-1}$	Specific heat capacity for liquid phase
c_{ps}	620	$\text{J kg}^{-1}\text{K}^{-1}$	Specific heat capacity for solid phase
k_l	60	$\text{W m}^{-1}\text{K}^{-1}$	Thermal conductivity for liquid phase
k_s	30	$\text{W m}^{-1}\text{K}^{-1}$	Thermal conductivity for solid phase
T_{cast}	1810	K	Initial alloy temperature
T_{sol}	1513	K	Melting temperature
T_0	300	K	Room temperature
ΔH_f	270000	J kg^{-1}	Latent heat
ρ_l	7000	kg m^{-3}	Liquid density
ρ_s	7800	kg m^{-3}	Solid density

Table 2 – Physical properties used for pipe-formation numerical simulation.

In order to consider the imposition of a hot-top defined in the upper part of the ingot, as mentioned in the section 3.1, a lower heat transfer coefficient is defined for this boundary representing the thermal insulation provided by this layer

$$h = 120 \text{ Wm}^{-2}\text{K}^{-1},$$

in the same relation as defined by eq. 3.12. The other parameters of the tested material were defined in Table 2.

Tests were carried out to estimate the total solidification time in steel ingots. Furthermore, from the imposition of a hot-top one can observe how this technique changes the solidification

Figure 3.6 – Contraction cavities for 4.2 ton ingot. To the right without using the hot-top and to the left with 20cm hot-top from the top, along the mould wall.

time, as described in Table 3. The final time obtained for the case in which the appearance of the cavity is considered is close to the value obtained in the reference. In general, there was a decrease in the total solidification time due to the inclusion of the shrinkage cavity (as in the rows 1-2, 3-4), and an increase in that time due to the effects of hot-top (rows 1-3-5).

Contraction	Hot-top[cm]	Solid. time[s]
No	-	7.811,5
Yes	-	7.408,3
No	20cm	9.111,2
Yes	20cm	7.881,1
No	33cm	9.688,4
Yes	20cm	8.040,0 ^(*)

Table 3 – Solidification time for 4.2 ton steel ingots with shrinkage cavity. (*) Data from (RAIHLE; FREDRIKSSON, 1993).

In order to visualize the effects of hot-top on the shape of the contraction cavity, simulations were performed with or without the apparatus and the result is shown in Fig. 3.6. Thus, a reduction of more than 25 % in the height of this cavity can be seen from the use of this technique. In addition, it is noticed that the solid layer adjacent to the wall takes longer to be formed when a certain degree of thermal insulation was imposed, as initially expected.

Fig. 3.7 shows the cavity profile considering different values of heat transfer coefficient h , attesting that increasing the insulation, thus decreasing the coefficient, leads to a decrease in the final pipe depth. Observe that a perfect insulation ($h = 0$) leads to the formation of a upper surface more or less planar. In Fig. 3.8, considering the standard coefficient, it is verified that the hot-top length (D) should at least be as great as the predicted cavity depth, from that point an apparatus of higher dimensions should have no positive effects on mitigating the cavity formation.

The maximum temperature found in the domain can be written over time, as illustrated in Fig. 3.9(a). Here, there is an unexpected oscillation at the start of the solidification process

Figure 3.7 – Shrinkage cavity profiles for different values of heat transfer coefficient, $D = 33$ cm.

Figure 3.8 – Shrinkage cavity profiles for different values hot-top length, $h = 120$ $\text{W/m}^2\text{K}^{-1}$.

Figure 3.9 – (a) Maximum temperature obtained in the computational domain for ingots of 4.2 ton over time, and (b) Oscillation on the temperature curve for different mesh sizes.

explained in Fig. 3.9(b), easily solved by the mesh refinement, without significant increase to the total solidification time.

Figure 3.10 – Temperature curve over time for 4.2 ton ingot in two mesh sizes.

A comparison of maximum temperature curve over time for different mesh refinements is shown in Fig. 3.10.

Mesh	N. elements	RAM	Duration	Solid. time [s]
Normal	14,887	990MB	32min	9,111
Normal	182,756	1.36GB	3hrs 52min	9,101

Table 4 – Solidification time, computing time, and memory requirements for different mesh sizes.

Table 4 shows the computing time and memory necessary to run the model for two different mesh refinements. Despite the increase in computing requirements, the final solidification time remains unaltered. All computations were carried out on a laptop with an Intel Core i7-3610M CPU 2.30GHz processor and 8GB RAM.

SINGLE DOMAIN MODELLING

In this chapter, the constitutive equations valid for the single domain approach, based on the set of equations defined in (AMBERG, 1991), are summarized in Section 4.1 with their respective boundary conditions and nondimensionalized in Section 4.2, in an attempt to reproduce the results in the original paper. A detailed discussion around this model has been presented in Section 2.2 of the Literature Review.

The computational simulation has been done using an in-house code developed in MATLAB that implements the Marker and cell Method described in Section 4.3, with numerical results presented in Section 4.4.

Figure 4.1 – Phase diagram for Fe-C alloy.

4.1 Mathematical Formulation

The phase diagram in Fig. 4.1 refers to a binary Fe-C system, which was the one considered by (AMBERG, 1991) and is the one that will be considered here. The two-dimensional domain consists in a rectangular cross section of an ingot with width $2W$ and height L . The side walls are cooled and the top and bottom surfaces are insulated. Horizontal symmetry is assumed so that the computational domain is reduced to $0 < x < W$, $0 < y < L$, as shown in Fig. 4.2.

Figure 4.2 – Mould geometry for single-domain formulation.

The system of equations valid throughout the domain consists in

$$\left\{ \begin{array}{ll} \rho_0 \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) - \mu \nabla^2 \mathbf{u} = -\nabla p - \rho g \mathbf{e}_y - \frac{\mu}{H(\chi)} \chi \mathbf{u}, & (4.1a) \\ \rho_0 c_p \left(\frac{\partial T}{\partial t} + \chi \mathbf{u} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) - \Delta H_f \frac{\partial \chi}{\partial t}, & (4.1b) \\ \frac{\partial c_m}{\partial t} + \nabla \cdot (\mathbf{u} \chi c_l) = D \nabla^2 c_m, & (4.1c) \\ \nabla \cdot (\chi \mathbf{u}) = 0, & (4.1d) \\ \frac{\partial \chi}{\partial t} = \frac{1}{\varepsilon} (T - T_l(c_l)), & (4.1e) \end{array} \right.$$

where T is the temperature, χ is the liquid fraction, $\mathbf{u}$ is the velocity vector, c_m is the mixture solute concentration. Subject to the boundary conditions

$$\left\{ \begin{array}{ll} u = v = 0 & \text{at } x = 0, y = 0, y = L, \\ u = \frac{\partial v}{\partial x} = 0 & \text{at } x = W, \\ -k \frac{\partial T}{\partial \mathbf{n}} = -Q & \text{at } x = 0 \\ \frac{\partial T}{\partial \mathbf{n}} = 0 & \text{at } x = 0, x = W, y = 0, y = L, \\ \frac{\partial c_m}{\partial \mathbf{n}} = 0 & \text{at } x = 0, x = W, y = 0, y = L, \end{array} \right. \quad (4.2)$$

and to the supplementary empirical relations

$$\begin{cases} \rho = \rho_0(1 + \alpha'(T - T_0) + f \cdot c_l), & (4.3a) \\ \alpha' = \frac{d}{e + 100c_l}, & (4.3b) \\ H(\chi) = Z_1 K_1 + Z_2 K_2, & (4.3c) \end{cases}$$

with experimentally measured constants d, e, f, Z_1, Z_2 , as described in Section 2.2. And initial conditions $\mathbf{u} = 0, T = T_{\text{ini}}, c_l = c_{\text{ini}}, \chi = 1$.

4.2 Nondimensionalization

4.2.1 Momentum conservation (4.1a)

Applying the relation (4.3a) to eq. (4.1a), we obtain:

$$\begin{aligned} \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} - \frac{\mu}{\rho_0} \nabla^2 \mathbf{u} &= -\frac{1}{\rho_0} \nabla p - \frac{\mu}{\rho_0} \frac{\chi}{H(\chi)} \mathbf{u} - g \mathbf{e}_y \\ &\quad + (1 + \alpha'(T - T_0) + f c_l) g \mathbf{e}_y, \end{aligned} \quad (4.4)$$

where μ is the dynamic viscosity, related to the kinematic viscosity ν by the relation $\nu = \frac{\mu}{\rho_0}$.

Thus:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} - \nu \nabla^2 \mathbf{u} = -\frac{1}{\rho_0} \nabla p - \nu \frac{\chi}{H(\chi)} \mathbf{u} + (\alpha'(T - T_0) + f c_l) g \mathbf{e}_y. \quad (4.5)$$

In order to nondimensionalize the equations, let's set

$$X = \frac{x}{L}, \quad Y = \frac{y}{L}, \quad \tau = \frac{t}{[t]}, \quad \theta = \frac{T - T_0}{\Delta T}, \quad P = \frac{p}{[p]}, \quad \mathbf{U} = \frac{\mathbf{u}}{L/[t]}, \quad \mathcal{H} = \frac{H}{[H]}, \quad (4.6)$$

where $[t] = L^2/\alpha$, $[p] = \rho_0 \alpha^2 / L^2$ with $\alpha = k/\rho_0 c_p$, the reference permeability $[H] = H_R$, and the nondimensional gradient operator

$$\bar{\nabla} = \left\{ \frac{\partial}{\partial X}, \frac{\partial}{\partial Y} \right\}. \quad (4.7)$$

to rewrite the terms multiplying the Laplacian of velocity and the source terms to the right hand side, which allows to identify some dimensionless numbers recurrently found in the study of these equations and that play an important role in describing the behavior of heat transfer in fluids, such as the numbers of Prandtl, Rayleigh, Darcy, and Galilei, respectively:

$$Pr = \frac{\nu}{\alpha}, \quad Ra = \frac{L^3 \alpha' \Delta T g}{\alpha \nu}, \quad Da = \frac{H_R}{L^2}, \quad Ga = \frac{L^3 g}{\nu^2}. \quad (4.8)$$

Applying these relations to the equation (4.5), we obtain:

$$\frac{\partial \mathbf{U}}{\partial \tau} + \mathbf{U} \cdot \bar{\nabla} \mathbf{U} - Pr \bar{\nabla}^2 \mathbf{U} = -\bar{\nabla} P - \frac{Pr}{Da} \frac{\chi}{\mathcal{H}(\chi)} \mathbf{U} + (Ra Pr \alpha' \theta + Ga Pr^2 f c_l) \mathbf{e}_y. \quad (4.9)$$

4.2.2 Heat conservation (4.1b)

Nondimensionalizing using the variables set in (4.6) and using the Stefan number

$$St = \frac{c_p \Delta T}{\Delta H_f}, \quad (4.10)$$

leads to

$$\frac{\partial \theta}{\partial \tau} + \chi \mathbf{U} \cdot \bar{\nabla} \theta = \bar{\nabla}^2 \theta - \frac{1}{St} \frac{\partial \chi}{\partial \tau}. \quad (4.11)$$

4.2.3 Solute and mass conservation (4.1c, 4.1d)

Nondimensionalizing using the variables set in (4.6) and using the Lewis number

$$Le = \frac{\alpha}{D} \quad (4.12)$$

leads to

$$\frac{\partial c_m}{\partial \tau} + \mathbf{U} \chi \bar{\nabla} c_l - \frac{1}{Le} \bar{\nabla}^2 c_l = 0, \quad (4.13)$$

where $c_l = \frac{c_m}{\chi + (1 - \chi)K_p}$. The mass conservation neglecting the shrinkage results in

$$\bar{\nabla} \cdot (\chi \mathbf{U}) = 0. \quad (4.14)$$

4.3 Numerical implementation

The methodology adopted in this step was to use the MAC Method (*Marker and cell Method*) to solve the proposed problem. Its fundamental characteristic is the spatial discretization using the finite volume method in a staggered grid, the momentum equation is solved by decoupling the resolution for the velocities and the pressure by the Projection Method, while for the temporal integration an Adams-Bashforth-Crank-Nicolson method is used. The discretization follows the method proposed in (PROSPERETTI; TRYGGVASON, 2007) and (BUSCAGLIA, 2015), with centered volume of control for each variable of the problem: u , v , p , T , c , as illustrated in Figure 4.3.

To implement the boundary conditions for velocity, the boundary position in the computational domain (Fig. 4.3) is taken into account in relation to the volume control of the velocities u and v . There are two types of treatment for the properties close to the contours. Consider the u -velocity as an example. In the first case, Fig. 4.4, it is necessary to use ghost points so that $u_{NN} = 2u_{bond} - u_p \Rightarrow u_{NN} = -u_p$.

Figure 4.3 – Staggered grid showing computational domain and different cells for each variable.

Figure 4.4 – Discretization of u -velocity near the wall. North boundary on the top, West boundary on the bottom.

is known that $\frac{\partial \theta}{\partial X} \Big|_{bond} = const$ and applying centered differences we get $\frac{\theta_p - \theta_{WW}}{h_x} = const$, therefore, $\theta_{WW} = \theta_p - h \cdot const$.

The other case occurs when the velocity u is over the domain boundary, as can be seen in Fig. 4.4. In this case, $u_{WW} = 0$ in the discretization of the u Laplacian.

For the case of temperature and concentration it is necessary to use a ghost point. At borders where the boundary condition is of the Neumann type, this information is used to assign a value to the point outside the domain. In the control volumes adjacent to the left and right walls, the calculations are analogous.

Therefore, consider a control volume close to the left wall. From the boundary condition it

4.4 Numerical Results

The solution for the nondimensionalized set of equations and adequate boundary conditions was approximated by computational simulation applying the presented methodology in a domain 20 cm wide and 10 cm high, with insulated top and bottom walls, cooling from the sides at the same given rate Q . Thus, horizontal symmetry is assumed and the dependent variables: temperature, pressure, velocities, concentration and liquid fraction are computed for just half of the original domain. The parameters used in the simulation can be found in Table 5 and in the Fe-C phase diagram. The resulting liquid fraction after 200s of solidification is shown in Figs. 4.5 with contour lines drawn across the domain.

	Value	Unit
c_p	753	$\text{J Kg}^{-1} \text{K}^{-1}$
D	1e-9	m^2s^{-1}
d	-4.2e-4	-
e	0.55	-
ε	1e-6	-
f	-8	-
g	9.8	ms^{-2}
m	7800	$\text{K/wt\%}$
k_l	30	$\text{W m}^{-1}\text{K}^{-1}$
L	0.1	m
W	0.1	m
ΔH_f	2.72e5	J kg^{-1}
H_R	1.5e-10	m^2
μ	6.94e-3	N s m^{-2}
ρ_0	6940	kg m^{-3}
Q	60	kW m^{-2}
T_0	1811	K
T_{ini}	1738	K
c_{ini}	1	wt%
Ga	9.8e9	
Ra	2.3e6	
Le	5.7e3	
Pr	1.7e-1	
St	1.3e-2	
Da	1.5e-8	

Table 5 – Physical parameters adopted on single-domain model.

Figs. 4.6 compares the mixture solute composition of the binary Fe-C alloy after 6000s of solidification, both images show noticeable differences in concentrations obtained across the domain, with lower concentration at the bottom and higher concentration at the top. Fig. 4.7.a illustrates the deceleration of the velocity field for the region with lower liquid fraction, while Fig. 4.7.b shows the corresponding streamlines.

Figure 4.8 – Mixture solute concentration comparison for different mesh sizes.

A mesh independence study was carried out using four different mesh refinements. Fig. 4.8 presents the contour lines for the internal elements solute concentration, obtained using an increasing number of elements. Here, h denotes the width of each square element that composes the grid. The computations were carried out until the infinity norm of the changes in concentration profile dropped below a critical value, here chosen as $1e-10$. It can be observed that the contour lines are on top of each other for refinements below $h = 1e-2$.

Increasing the number of elements leads to an increment on the computing time, as shown by the data presented in Table 6, where the column Duration refers to the elapsed time needed to obtain the profiles presented in Fig. 4.8, and the time decrease is based on the longest computation. The time measurement was done by Matlab built-in functions *tic*, *toc*. All computations were carried out on a laptop with an Intel Core i7-9750HQ CPU 2.60GHz processor and 16GB RAM.

h	N. elements	Duration	Time decrease [%]
1.25e-3	6724	9d 10hrs 47min	0.00
2.50e-3	1764	1d 4hrs 49min	87.29
5.00e-3	484	10hrs 24min	95.41
1.00e-2	144	58min	99.57

Table 6 – Mesh sizes with uniform element size h , number of elements and the time it took to obtain the results compared in Fig. 4.8.

In general, it is noted that regions with certain liquid fraction rates are distributed along the domain in an expected manner, while macrosegregation has been observed in the results, as

well as in the original article: above average concentration in the upper portion of the domain, and below-average concentration in the lower portion.

Fig. 4.9 shows the effects of the artificial parameter ϵ in equation 2.26 on the solute concentration profile, here we can observe that choosing the arbitrary constant ϵ greater than $1e-4$ leads to significant changes in the location and severity of concentration deviations, reaffirming the understanding that ϵ should be taken as small as possible.

As discussed in Section 5.5.2, the degree of accuracy in eq. (2.25) is expected to be proportional to ϵ . At the same time, comparing T and T_L is presented by Amberg as an option to monitor the actual error in the computations. Accordingly, Table 7 can numerically confirm both relationships, while implying, not surprisingly, that increased accuracy by reducing ϵ incurs in higher computing times

In the table, computing times are compared with the one obtained for the lowest ϵ , while the numerical errors are calculated using two formulas

$$E_L = \frac{\|T - T_L\|_2}{\|T_L\|_2}, \quad E_R = \frac{\|T - T_R\|_2}{\|T_R\|_2},$$

where $\|\cdot\|_2$ is the 2-norm, and the temperature profile obtained for the lowest ϵ is adopted as the reference value T_R . All the results were obtained using a time step $dt = 1e-8$. Decreasing ϵ below that point leads to convergence problems, as expected and already pointed out in Section 5.5.2. Amberg also argued that the allowable values of ϵ would typically result in an error of less than 0.15% of the typical temperature variation over the mush, which was also verified numerically.

Figure 4.9 – Mixture solute concentration comparison for different values of ϵ .

ε	Time decrease [%]	E_L	E_R
1e-6	0.00	3.50e-7	0.00
1e-4	7.20	2.90e-5	2.23e-5
1e-2	14.58	2.89e-3	2.26e-3
1e-1	15.44	2.89e-2	2.28e-2

Table 7 – Accuracy and decrease in computing times for increasing values of ε . Considering $h = 5e-3$.

4.4.1 Final considerations

The single domain model provides the interesting advantage of not having to track the moving interfaces between the different domains. However, as we can observe from the previous results and from the considerations in Section 2.2, it comes at the high expense of incorporating a seemingly artificial numerical parameter, which will have negative effects on the solution accuracy and potentially defile its physical meaning. Besides that, meeting the requirements for an ε “small enough” incurs into elevated computing costs, adding to the penalty of numerically correcting the liquid fraction that may be changed out of the physical range.

Due to the nature of the problem verifiable in the parameters table, the convective term dominates the solute transport throughout the domain. Even though the mass diffusivity is high enough to smooth out variations on the dendrite length scale, the diffusive transport is negligible when compared to the convective transport on macroscopic scale. It is also clear that change in volume due to solidification is neglected in this model.

In the next Chapter, a model is proposed to trade the costs of tracking the moving boundaries for improved numerical and physical accuracy, combined with the analysis that leads to semi-analytical solutions and provides important insights into the solution structure. In many aspects, the model can be seen as an extension to existing works in the literature.

MULTI-DOMAIN MODELLING

In this chapter, the model described in Section 5.1 is nondimensionalized before using a triple Landau transformation in Section 5.3 to reformulate the equations, which are then analyzed in the small-time limit, leading to a system of similarity ordinary differential equations; the solutions to these, which must be obtained numerically, are presented in Section 5.5.

5.1 Mathematical Formulation

The originality of this model consists on incorporating the mass, momentum, and energy balance equations over a finite domain with three moving boundaries applied to the study of macrosegregation problem. While other authors, as described in Section 2.3, opted for ruling out at least one of those aspects.

Although highly idealized, the one-dimensional problem for the solidification of a cooling binary alloy melt which simultaneously undergoes solidification shrinkage is important for a number of reasons. In this situation, a melt velocity is induced and this is therefore the simplest configuration in which to examine the role of convection in a binary system.

Moreover, this configuration is believed to permit a similarity solution to the governing equations (CHAKRABORTY; DUTTA, 2002; JAKHAR; RATH; MAHAPATRA, 2016; VOLLER, 1997; WACLAWCZYK; SCHäFER, 2018), which can then be used as a benchmark for testing higher-dimensional numerical codes. Furthermore, the fact that there is relative motion between solid and liquid phases in the so-called mushy zone, where the two phases coexist, leads to the possibility of macrosegregation (CHEN; TSAI, 1993; DIAO; TSAI, 1993a; DIAO; TSAI, 1993b; MINAKAWA; SAMARASEKERA; WEINBERG, 1985; MO, 1993).

Within the scope of the present work, following (VOLLER; BRENT; PRAKASH, 1989), it is assumed that the system has already undergone the Mullins–Sekerka instability, differently from what is assumed in other works (PLANELLA; PLEASE; GORDER, 2019),(FELTHAM;

Figure 5.1 – Solidification with shrinkage: (a) initial configuration at $t = 0$; (b) after time $t > 0$

[GARSIDE, 2001](#)). In the first approach, it is considered that the instability creates a region that occupies a representative volume and contains solid dendrites and interdendritic melt, the mushy zone. This approach presumes the existence of two interfaces separating the solid from mush and the mush from the liquid. In the second approach, the moving interface between the solid phase and the molten phase has a planar profile and separates the two regions where solid dendrites and melt do not coexist.

From this point on, the governing equations are formulated for the temperature, liquid fraction, and solute concentration using a three-regions, transient, one-dimensional approach, as shown in Fig. 5.1, in which a region of binary alloy melt of finite initial extent l , temperature T_{cast} and composition C_0 , is cooled by a boundary at $y = 0$ that is held at temperature T_w . To fix ideas more precisely, it is supposed that the alloy in question has a phase diagram with an eutectic point, with eutectic temperature and concentration T_{eut} and C_{eut} respectively, as indeed is the case for many alloys of technological interest. Fig. 5.2 shows the phase diagram for the Al-Cu system, which was the one implicitly considered by [VOLLER, 1997](#) and the one that will be considered here as well as the parameters presented in Table 8. It is also assumed that $T_w < T_{\text{eut}}$, which ensures that complete solidification occurs for any choice of C_0 , such that $0 \leq C_0 \leq C_{\text{eut}}$.

As indicated in Fig. 5.1, at some time $t > 0$, the region that initially occupied $0 \leq y \leq l$ will shrink to occupy $0 \leq y \leq y_\infty(t)$, which consists of a solid region occupying $0 \leq y \leq y_s(t)$, a mushy zone occupying $y_s(t) \leq y \leq y_l(t)$ and the melt region occupying $y_l(t) \leq y \leq y_\infty(t)$; the shrinkage occurs as a result of phase change, as molten region begins to solidify, with the density of the solid being greater than that of the molten phase. The governing equations are considered for each region in turn.

Figure 5.2 – Al-rich side of the linearized phase diagram for the Al-Cu system. L denotes liquid phase, and α and θ denote two solid phases.

	Value	Unit
c_{pl}	1107	$\text{J kg}^{-1}\text{K}^{-1}$
c_{ps}	1107	$\text{J kg}^{-1}\text{K}^{-1}$
C_0	5	wt%
g	9.81	ms^{-2}
k_l	100	$\text{W m}^{-1}\text{K}^{-1}$
k_s	100	$\text{W m}^{-1}\text{K}^{-1}$
k_0	0.17	-
L	0.15	m
m	3.37	$\text{K/wt\%}$
T_{cast}	943	K
T_{liq}	916	K
T_m	933	K
T_{sol}	836	K
T_w	621	K
W	0.025	m
κ_0	10^{-11}	m^2
μ	0.007	$\text{kg m}^{-1}\text{s}^{-1}$
ρ_l	2400	kg m^{-3}
ρ_s	2550	kg m^{-3}
ΔH_f	392000	J kg^{-1}

Table 8 – Parameters for computations for Al-5 wt% Cu

5.1.1 Solid region

Following Carslaw and Jaeger (CARSLAW; JAEGER, 1959), in order to formulate the equation that expresses the temperature in the solid domain, besides the temperature itself, other two fundamental quantities in heat conduction are going to be used: enthalpy and heat flux, which are related to temperature by

$$dh = c_p dT, \quad (5.1)$$

$$\mathbf{q} = -k \nabla T, \quad (5.2)$$

where h is the enthalpy – the quantity of heat absorbed by unit of mass under constant pressure, and measured in kJ/kg, and c_p is the specific heat. In eq. (5.2), $\mathbf{q}$ represents the heat flux – the amount of heat crossing a unit area per unit time - measured in kW/m K and defined by Fourier's second law, where k represents the thermal conductivity. Further descriptions on these properties have already been given in section 2.2.

Enthalpy and heat flux are related by the fundamental law of conductive heat transfer, known as energy conservation law,

$$\frac{\partial(\rho h)}{\partial t} + \nabla \cdot \mathbf{q} = F, \quad (5.3)$$

where ρ is the material density and F is the volumetric heat source, measured in kJ/m³s (ALEXIADES, 1992; CARSLAW; JAEGER, 1959), which can be understood as the differential form of the first law of thermodynamics:

$$\frac{d}{dt} \int_V \rho h dV = \int_V F dV - \int_A \mathbf{q} \cdot \mathbf{n} dS, \quad (5.4)$$

where V represents an arbitrary volume, S is the surface and $\mathbf{n}$ is the normal to A . From eq. (5.4), replacing the surface integral by a volume integral, we obtain

$$\frac{d}{dt} \int_V \rho h dV = \int_V F dV - \int_V \nabla \cdot \mathbf{q} dV, \quad (5.5)$$

now substituting eq. (5.1–5.2) into equation 5.3, leads to the heat conduction equation

$$\rho c_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = F. \quad (5.6)$$

Considering zero internal heat generation and one-dimensional domain, we obtain for the solid phase

$$\rho_s c_{ps} \frac{\partial T}{\partial t} = k_s \frac{\partial^2 T}{\partial y^2}, \quad (5.7)$$

where ρ_s , c_{ps} and k_s are the density, specific heat capacity and thermal conductivity, respectively, of the solid phase, all of which are assumed to be constant.

5.1.2 Mush

The total mass balance equation over solid and liquid phases in the mush region, is derived from summing the phase conservation equations as in (BENNON; INCROPERA, 1987). First, let's consider the conservation of a scalar quantity ϕ , as a balance of accumulation, convection and diffusion outflow and production/depletion over a control volume V and surface area A , as

$$\frac{\partial}{\partial t} \int_V (\rho_i \phi_i) dV_i + \int_A (\rho_i \mathbf{U}_i \phi_i) \cdot \mathbf{n} dA_i = \int_A -\mathbf{J} \cdot \mathbf{n} dA_i + \int_V F_i dV_i, \quad (5.8)$$

where i denotes each of the phases in the mush, ρ is the material density, $\mathbf{n}$ is the outward normal to the surface, $\mathbf{U}_i$ is the phase velocity, $\mathbf{J}_i$ is the surface flux and F_i is the source term. Writing eq. (5.8) in differential form, and considering the volume fraction g_i such that $dA_i = g_i dA$, leads to

$$\frac{\partial}{\partial t} (\rho_i g_i \phi_i) + \nabla \cdot (\rho_i g_i \mathbf{U}_i \phi_i) = -\nabla \cdot (g_i \mathbf{J}_i) + g_i F_i. \quad (5.9)$$

From eq. (5.9), using $\phi_i=1$, $F_i = M_i$ and zero mass outflow, we obtain the conservation of mass for each phase:

$$\frac{\partial}{\partial t} (\rho_i g_i) + \nabla \cdot (\rho_i \mathbf{U}_i) = g_i M_i. \quad (5.10)$$

Now summing over the eq. (5.10) for liquid and solid phases, and considering that the production of the solid phase depends on the depletion of the liquid phase, we get

$$\sum_i \frac{\partial}{\partial t} (\rho_i g_i) + \sum_i \nabla \cdot (\rho_i \mathbf{U}_i) = 0, \quad (5.11)$$

with the liquid fraction $g_l = \chi$ and the solid fraction $g_s = 1 - \chi$, thus, in one-dimensional form

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial y} (\rho_l \chi v) = 0, \quad (5.12)$$

where ρ_l is the density of the liquid phase, and with the mass-averaged velocity consisting only of the liquid phase velocity, v , since the solid does not move and its velocity is therefore zero. Also, ρ is the mixture density which, following (VYNNYCKY; SALEEM; FREDRIKSSON, 2018), is written in terms of the liquid fraction, χ , as

$$\rho = \chi \rho_l + (1 - \chi) \rho_s; \quad (5.13)$$

equation (5.12) can then be written as

$$(1 - R) \frac{\partial \chi}{\partial t} + \frac{\partial U}{\partial y} = 0, \quad (5.14)$$

with the density ratio

$$R = \rho_s / \rho_l, \quad (5.15)$$

and velocity $U = \chi v$.

Adopting the same procedure, the continuum equation for conservation of energy may also be obtained from the summation of the energy conservation for each phase i . Starting from eq. (5.9), setting $\phi = h$, where h is the enthalpy, $F_i = E_i$, and $\mathbf{J} = -k_i \nabla T$, we get for each phase

$$\frac{\partial}{\partial t}(\rho_i g_i h_i) + \nabla \cdot (\rho_i g_i \mathbf{U}_i h_i) = \nabla \cdot (g_i k_i \nabla T) + g_i E_i. \quad (5.16)$$

Following Alexiades (ALEXIADES, 1992), in the mushy region the release of latent heat is accounted for by a heat source term equal to $\frac{\partial}{\partial t}(\rho \Delta H_f g_l)$, again with the liquid fraction $g_l = \chi$ and solid fraction $g_s = 1 - \chi$ with zero velocity for solid phase and recalling eq. (5.1) for the enthalpy, we get in the one-dimensional form

$$\frac{\partial}{\partial t}(\rho_s c_{ps}(1 - \chi)(T - T_{\text{ref}})) = \frac{\partial}{\partial y} \left(k_s(1 - \chi) \frac{\partial T}{\partial y} \right), \quad (5.17)$$

$$\frac{\partial}{\partial t}(\rho_l c_{pl} \chi (T - T_{\text{ref}})) + \frac{\partial}{\partial y}(\rho_l c_{pl} U (T - T_{\text{ref}})) = \frac{\partial}{\partial y} \left(k_l \chi \frac{\partial T}{\partial y} \right) - \Delta H_f \frac{\partial}{\partial t}(\rho_l \chi), \quad (5.18)$$

where c_{pl} and k_l denote the specific heat capacity and thermal conductivity, respectively, of the liquid phase, while c_{ps} and k_s denote the same quantities of the solid phase, and ΔH_f is the latent heat of fusion. Adding eq. (5.18) to eq. (5.17), leads to the conservation of energy given by

$$\frac{\partial}{\partial t}(\{\rho_l c_{pl} \chi + \rho_s c_{ps}(1 - \chi)\}(T - T_{\text{ref}})) + \frac{\partial}{\partial y}(\rho_l c_{pl} U (T - T_{\text{ref}})) = \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) - \Delta H_f \frac{\partial}{\partial t}(\rho_l \chi), \quad (5.19)$$

where k is the mixture thermal conductivity, written as

$$k = \chi k_l + (1 - \chi) k_s. \quad (5.20)$$

Although this is arguably not the most natural mixture rule, which would be based on the reciprocal of conductivities, it is nevertheless one that is frequently used (AMBERG, 1991; VOLLER; BRENT; PRAKASH, 1989; VYNNYCKY; SALEEM; FREDRIKSSON, 2018). Also, T_{ref} is a reference temperature, to which thermal energies in all phases must refer consistently; a convenient choice for T_{ref} is T_m , the melting point of the solvent element.

The equation for the conservation of solute is obtained from eq. (5.8), by setting the scalar quantity as the mixture concentration, neglecting the diffusive transport at the macroscale ($\mathbf{J} = 0$), and the source term $F_i = S_i$, we get

$$\frac{\partial}{\partial t}(\rho_i g_i \phi_i) + \nabla \cdot (\rho_i g_i \mathbf{U}_i \phi_i) = g_i S_i. \quad (5.21)$$

However, the result of the product $g_i \phi_i$ for the solid phase depends on the assumption made regarding solute transport at the microscale. The two extremes are the lever rule and the Scheil equation (JALANTI *et al.*, 2006; SWAMINATHAN; VOLLER, 1997; VOLLER; SUNDARRAJ, 1995; XIONG; KUZNETSOV, 2001), where

$$g_s \phi_s = \begin{cases} \rho_s (1 - \chi) C_s, & \text{lever rule} \\ \rho_s \int_0^{1-\chi} C_s d\chi', & \text{Scheil equation} \end{cases}, \quad (5.22)$$

As the source term S_i represents the production of solute in the solid phase at the expense of solute depletion in the liquid phase, by summing the conservation equations over both phases we obtain at the right-hand side $\sum_i g_i S_i = 0$. Also, recalling that the solid velocity is zero, the continuum solute conservation equation is given by

$$\frac{\partial}{\partial t}(\rho C) + \frac{\partial}{\partial y}(\rho_l C_l U) = 0, \quad (5.23)$$

where the form for the mixture concentration, C , according to eq. (5.22) is

$$\rho C = \chi \rho_l C_l + \begin{cases} \rho_s (1 - \chi) C_s, & \text{lever rule} \\ \rho_s \int_0^{1-\chi} C_s d\chi', & \text{Scheil equation} \end{cases}, \quad (5.24)$$

with C_l and C_s as the concentrations of the solute in the liquid and solid phases, respectively, which are related by

$$C_s = k_0 C_l, \quad (5.25)$$

where k_0 is the partition coefficient. Moreover, the lever rule assumes thermodynamic equilibrium between the phases, whereas the Scheil rule, also known as the non-equilibrium lever rule, assumes no solute diffusion in the solid and perfect mixing in the liquid (ALEXIADES, 1992). For the purposes of generalization, it is possible to introduce a parameter β , where $0 \leq \beta \leq 1$, that allows for a back-diffusion treatment, i.e. partial solute diffusion into the solid, that lies between the limits of zero back diffusion ($\beta = 0$, the Scheil assumption) and complete back diffusion ($\beta = 1$, the lever rule); as indicated in (SWAMINATHAN; VOLLER, 1997), this treatment of back diffusion is equivalent to using the Clyne and Kurz correction (CLYNE; KURZ, 1981) of the well-known back diffusion model of (BRODY; FLEMINGS, 1966). Following (SWAMINATHAN; VOLLER, 1997) in first setting

$$\int_0^{1-\chi} \frac{\partial C_s}{\partial t} d\chi' = \beta (1 - \chi) k_0 \frac{\partial C_l}{\partial t}, \quad (5.26)$$

equation (5.23) becomes

$$\rho_l \frac{\partial}{\partial t}(\chi C_l) - k_0 \rho_s C_l \frac{\partial \chi}{\partial t} + \rho_s \beta (1 - \chi) k_0 \frac{\partial C_l}{\partial t} + \frac{\partial}{\partial y}(\rho_l C_l U) = 0; \quad (5.27)$$

furthermore, we note that (5.24) can now be generalized for $0 \leq \beta \leq 1$ to

$$\rho C = \chi \rho_l C_l + \rho_s \int_0^{1-\chi} \left(C_s + \beta \chi' \frac{dC_s}{d\chi'} \right) d\chi'. \quad (5.28)$$

Moreover, the local thermodynamic equilibrium in the mushy region is assumed, so that, from the liquidus line in the phase diagram,

$$T = T_m - m C_l \quad \text{for } 0 \leq \chi \leq 1, \quad (5.29)$$

where $m > 0$; note here that, in view of the minus sign in equation (5.29), the slope of the liquidus line in the phase diagram will be $-m$.

5.1.3 Melt region

Here, the mass balance can be written just as

$$\frac{\partial U}{\partial y} = 0, \quad (5.30)$$

which can be thought of as the result of setting $\chi = 1$ in equation (5.14).

The conservation of energy is given by

$$\rho_l c_{pl} \left(\frac{\partial}{\partial t} (T - T_{\text{ref}}) + \frac{\partial}{\partial y} (U (T - T_{\text{ref}})) \right) = k_l \frac{\partial^2 T}{\partial y^2}, \quad (5.31)$$

also derived considering $\chi = 1$ in equation (5.19), while neglecting changes in material properties inside the melt region, whereas the conservation of solute, as in (FLEMINGS, 1974), is given by

$$\frac{\partial}{\partial t} (\rho_l C_l) + \frac{\partial}{\partial y} (\rho_l C_l U) = 0. \quad (5.32)$$

For simplicity, let's henceforth set $c_{ps} = c_{pl}$ and $k_s = k_l$, although keeping $\rho_s \neq \rho_l$ throughout.

5.1.4 Boundary and interface conditions

In this section the boundary and interface conditions are going to be discussed as a part of the multi-domain modelling. The task of tracking the interfaces between the solid, mush and liquid regions is, in some terms, relatable to the widely studied moving boundary problems known as Stefan problem, which has been extended over the past century in order to be applied to solidification of alloy systems, among other applications (ALEXIADES, 1992). An extended discussion on this topic has been presented in Section 2.4.

5.1.4.1 Heat and solute

At $y = 0$, we have

$$T = T_w, \quad (5.33)$$

as implied by the discussion at the beginning of Section 5.1.

Negligible heat loss at the upper surface of the melt can be assumed, which is expressed by

$$\frac{\partial T}{\partial y} = 0 \quad \text{at } y = y_\infty(t). \quad (5.34)$$

Similarly, a condition is necessary on the solute concentration; analogous to (5.34), we take

$$\frac{\partial C_l}{\partial y} = 0. \quad (5.35)$$

An interface conditions is also required at $y = y_s(t)$ and $y_l(t)$. At $y = y_s(t)$, two of these - the continuity of temperature and a heat balance - are straightforward, and are given, respectively, by

$$[T]_{-}^{+} = 0 \quad \text{at } y = y_s(t), \quad (5.36)$$

$$\left[k \frac{\partial T}{\partial y} \right]_{-}^{+} = -\rho_l \Delta H_f \chi \frac{dy_s}{dt} \quad \text{at } y = y_s(t), \quad (5.37)$$

with $[]_{-}^{+}$ denoting the difference in the value of that function above and below $y = y_s(t)$; note that the value of k on the minus side in (5.37) is implicitly taken to be k_s . The relation (5.37) denotes the Stefan condition, which states that the rate of change in latent heat equals the amount by which the conductive heat flux jumps across the interface (ALEXIADES, 1992). Also, it is evident that the temperature on the mush side of this interface must satisfy (5.29), but this in itself does not provide a third condition, since C_l is not yet known. Considering first the limiting case of eutectic solidification, it is known that one should set $T = T_{\text{eut}}$, which will lead to $C_l = C_{\text{eut}}$, and that $\chi > 0$ at $y = y_s(t)$; the actual value of χ must be computed as part of the solution. On the other hand, if $C_l < C_{\text{eut}}$, then $\chi = 0$ at $y = y_s(t)$; in this case, neither T nor C_l are known *a priori*, although they are linked by (5.29), and must be computed. Moreover, for arbitrary values of the model parameters, it cannot be known beforehand whether C_l at $y = y_s(t)$ will reach C_{eut} or not. In summary,

$$\begin{cases} \chi = 0, & T = T_m - mC_l, & \text{if } C_l < C_{\text{eut}} \\ T = T_{\text{eut}}, & & \text{if } C_l = C_{\text{eut}} \end{cases} \quad \text{at } y = y_s(t), \quad (5.38)$$

indicating that two relations are required for the three dependent variables χ, T, C_l . Furthermore, let's henceforth set $\chi_s = \chi|_{y=y_s(t)}$.

At $y = y_l(t)$, we have the continuity of temperature and heat flux, so that

$$[T]_{-}^{+} = 0, \quad (5.39)$$

$$\left[k \frac{\partial T}{\partial y} \right]_{-}^{+} = 0, \quad (5.40)$$

where the value of k on the plus side in (5.40) is implicitly taken to be k_l , and, analogous to the first alternative in (5.38),

$$\chi = 1, \quad T = T_m - mC_l. \quad (5.41)$$

5.1.4.2 Mass

Boundary conditions for U are obtained by considering the global conservation of mass. For this, one has

$$\rho_s \int_0^{y_s(t)} dy + \int_{y_s(t)}^{y_l(t)} \rho dy + \rho_l \int_{y_l(t)}^{y_{\infty}(t)} dy = \rho_l \int_0^l dy, \quad (5.42)$$

which, on re-arranging and using (5.13), gives

$$(1 - R) \left\{ \int_{y_s(t)}^{y_l(t)} \chi dy - y_l(t) \right\} = \int_{y_\infty(t)}^l dy. \quad (5.43)$$

Differentiating (5.43) with respect to t and using Leibniz' rule gives

$$(1 - R) \left\{ \dot{y}_l(t) \chi(y_l(t)) - \chi_s \dot{y}_s(t) \chi_s + \int_{y_s(t)}^{y_l(t)} \frac{\partial \chi}{\partial t} dy - \dot{y}_l(t) \right\} = -\dot{y}_\infty(t), \quad (5.44)$$

whence

$$(1 - R) \left\{ \int_{y_s(t)}^{y_l(t)} \frac{\partial \chi}{\partial t} dy - \chi_s \dot{y}_s(t) \right\} = -\dot{y}_\infty(t); \quad (5.45)$$

using (5.14) gives

$$(1 - R) \left\{ \frac{1}{1 - R} \int_{y_s(t)}^{y_l(t)} \frac{\partial U}{\partial y} dy + \chi_s \dot{y}_s(t) \right\} = 0, \quad (5.46)$$

leading to

$$(U)_{y_s(t)} - (U)_{y_l(t)} = (1 - R) \chi_s \dot{y}_s(t) - \dot{y}_\infty(t). \quad (5.47)$$

Moreover, because U is continuous at $y = y_l(t)$, this will be the value used in (5.12). Note also that U in the melt satisfies

$$\frac{\partial U}{\partial y} = 0, \quad (5.48)$$

and implies that $U = U(t)$ there; furthermore, taking $U \neq 0$ in the melt is consistent with the analogous problem of the melting of a solid block, in which $U \neq 0$ in the as-yet unmelted solid (ALEXIADES, 1992). In fact,

$$(U)_{y_l(t)} = \dot{y}_\infty(t), \quad (5.49)$$

leading to

$$(U)_{y_s(t)} = (1 - R) \chi_s \dot{y}_s(t). \quad (5.50)$$

5.1.4.3 Initial conditions

For $y > 0$,

$$T = T_{\text{cast}}, \quad (5.51)$$

$$C_1 = C_0, \quad (5.52)$$

where the initial temperature T_{cast} is obtained from the liquidus temperature corresponding to the initial solute concentration plus the superheat

$$T_{\text{cast}} = T_{\text{liq}} + \delta T. \quad (5.53)$$

Initial-like conditions are required for y_l , y_s and y_∞ ; setting

$$y_l(0) = 0, \quad (5.54)$$

$$y_s(0) = 0, \quad (5.55)$$

$$y_\infty(0) = l. \quad (5.56)$$

Furthermore, these yield a further condition. Integrating (5.23) over $0 \leq y \leq y_\infty(t)$, we have

$$\int_0^{y_\infty(t)} \frac{\partial}{\partial t} (\rho C) dy = -[\rho_1 C_1 U]_0^{y_\infty(t)}.$$

Applying Leibniz' rule on the left-hand side, we have

$$\int_0^{y_\infty(t)} \frac{\partial}{\partial t} (\rho C) dy = \frac{\partial}{\partial t} \left(\int_0^{y_\infty(t)} \rho C dy \right) - \dot{y}_\infty(t) (\rho C)_{y_\infty(t)},$$

which results in just

$$\frac{\partial}{\partial t} \left(\int_0^{y_\infty(t)} \rho C dy \right) = 0.$$

Applying the initial conditions, we have

$$\int_0^{y_\infty(t)} \rho C dy = \rho_1 C_0 l; \quad (5.57)$$

note that this describes the conservation of solute over the whole system.

5.2 Nondimensionalization

In order to nondimensionalize the equations, let's define

$$Y = \frac{y}{l}, \quad \tau = \frac{t}{[t]}, \quad \theta = \frac{T - T_w}{T_{\text{cast}} - T_w}, \quad \hat{U} = \frac{U}{l/[t]}, \quad Y_s = \frac{y_s}{l}, \quad Y_l = \frac{y_l}{l}, \quad Y_\infty = \frac{y_\infty}{l}, \quad (5.58)$$

where $[t]$ is a timescale, which shall be assumed as being given by $[t] = \rho_1 c_{\text{pl}} l^2 / k_l$. In the solid:

$$R \frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial Y^2}; \quad (5.59)$$

in the mush,

$$\frac{\partial}{\partial \tau} (\chi + (1 - \chi) R) + \frac{\partial \hat{U}}{\partial Y} = 0, \quad (5.60)$$

$$[\chi + (1 - \chi) R] \frac{\partial \theta}{\partial \tau} + \hat{U} \frac{\partial \theta}{\partial Y} = \frac{\partial^2 \theta}{\partial Y^2} - \frac{R}{St} \frac{\partial \chi}{\partial \tau}, \quad (5.61)$$

$$\frac{\partial}{\partial \tau} (\chi C_l) - k_0 R C_l \frac{\partial \chi}{\partial \tau} + \beta R (1 - \chi) k_0 \frac{\partial C_l}{\partial \tau} + \frac{\partial}{\partial Y} (C_l \hat{U}) = 0, \quad (5.62)$$

$$\theta = \theta_m - \tilde{m} C_l, \quad (5.63)$$

where $St = c_{\text{pl}} (T_{\text{cast}} - T_w) / \Delta H_f$ and

$$\theta_m = \frac{T_m - T_w}{T_{\text{cast}} - T_w}, \quad \tilde{m} = \frac{m}{T_{\text{cast}} - T_w};$$

in the melt,

$$\frac{\partial \hat{U}}{\partial Y} = 0, \quad (5.64)$$

$$\frac{\partial \theta}{\partial \tau} + \hat{U} \frac{\partial \theta}{\partial Y} = \frac{\partial^2 \theta}{\partial Y^2}, \quad (5.65)$$

$$\frac{\partial C_1}{\partial \tau} + \frac{\partial}{\partial Y} (C_1 \hat{U}) = 0. \quad (5.66)$$

Note, incidentally, that there is no trace of any terms involving the reference temperature in equations (5.61) and (5.65), as these vanish as a consequence of (5.60) and (5.64) and the fact that $c_{ps} = c_{pl}$ was assumed.

The boundary and interfacial conditions are then: at $Y = 0$,

$$\theta = 0; \quad (5.67)$$

at $Y = Y_s(\tau)$,

$$\begin{cases} \chi = 0, & \theta = \theta_m - \tilde{m}C_1 & \text{if } C_1 < C_{\text{eut}} \\ \theta = \theta_{\text{eut}} & & \text{if } C_1 = C_{\text{eut}} \end{cases}, \quad (5.68)$$

$$\left[\frac{\partial \theta}{\partial Y} \right]_-^+ = -\frac{\chi_s}{S_l} \dot{Y}_s(\tau), \quad (5.69)$$

$$\hat{U} = (1 - R) \chi_s \dot{Y}_s(\tau), \quad (5.70)$$

where

$$\theta_{\text{eut}} = \frac{T_{\text{eut}} - T_w}{T_{\text{cast}} - T_w};$$

at $Y = Y_l(\tau)$,

$$\theta = \theta_m - \tilde{m}C_1, \quad (5.71)$$

$$\left[\frac{\partial \theta}{\partial Y} \right]_-^+ = 0, \quad (5.72)$$

$$\chi = 1; \quad (5.73)$$

at $Y = Y_\infty(\tau)$,

$$\frac{\partial \theta}{\partial Y} = 0, \quad (5.74)$$

$$\frac{\partial C_1}{\partial Y} = 0. \quad (5.75)$$

As for the initial conditions, for $0 < Y \leq 1$,

$$\theta = 1, \quad (5.76)$$

$$C_1 = C_0, \quad (5.77)$$

as well as

$$Y_l(0) = 0, \quad (5.78)$$

$$Y_s(0) = 0, \quad (5.79)$$

$$Y_\infty(0) = 1. \quad (5.80)$$

Also, from (5.57)

$$\int_0^{Y_\infty(\tau)} \rho C dY = \rho_l C_0. \quad (5.81)$$

5.3 Analysis

5.3.1 Transformed equations

As already mentioned, a similarity solution for general τ cannot be expected and, rather than expecting to be able to proceed in terms of the usual $Y/\tau^{1/2}$ similarity variable, a triple Landau transformation is introduced, with a view of immobilizing the three interfaces posing the problem on a fixed spatial domain, via

$$\eta = \begin{cases} Y/Y_s(\tau), & 0 < Y < Y_s(\tau) \\ 1 + \frac{Y - Y_s(\tau)}{Y_l(\tau) - Y_s(\tau)}, & Y_s(\tau) < Y < Y_l(\tau) \\ 2 + \frac{Y - Y_l(\tau)}{Y_\infty(\tau) - Y_l(\tau)}, & Y_l(\tau) < Y < Y_\infty(\tau) \end{cases} \quad (5.82)$$

and

$$\theta = F(\eta, \tau), \quad \hat{U} = \tau^{-1/2} \tilde{U}(\eta, \tau), \quad \chi = \chi(\eta, \tau), \quad C_l = C_l(\eta, \tau); \quad (5.83)$$

although transformation (5.82) may appear to complicate the subsequent algebra, it makes the behaviour of the governing equations in the limit as $\tau \rightarrow 0$ more transparent. Of note here is the supposition that $\hat{U}$ will behave as $\tau^{-1/2}$ as $\tau \rightarrow 0$. However, this is exactly the behaviour that was assumed in (VOLLER, 1997), and it will be found here also that it leads to a sensibly posed problem for $\tilde{U}$. Furthermore, it is the behaviour seen in the classical two-phase Neumann problem when the solid and liquid densities are different (ALEXIADES, 1992; CARSLAW; JAEGER, 1959), and is merely a natural consequence of the velocity of the solidification front itself behaving initially as $\tau^{-1/2}$, even when the solid and liquid densities are equal.

One will have: for $0 \leq \eta \leq 1$,

$$R \left(Y_s^2 \frac{\partial F}{\partial \tau} - \eta Y_s \dot{Y}_s \frac{\partial F}{\partial \eta} \right) = \frac{\partial^2 F}{\partial \eta^2}; \quad (5.84)$$

for $1 \leq \eta \leq 2$,

$$(1 - R) \left(\frac{\partial \chi}{\partial \tau} + \eta_\tau \frac{\partial \chi}{\partial \eta} \right) + \frac{1}{\tau^{1/2} (Y_l(\tau) - Y_s(\tau))} \frac{\partial \tilde{U}}{\partial \eta} = 0, \quad (5.85)$$

$$\begin{aligned}
& [\chi + (1 - \chi)R] \left(\frac{\partial F}{\partial \tau} + \eta_\tau \frac{\partial F}{\partial \eta} \right) + \frac{\tilde{U}}{\tau^{1/2} (Y_1(\tau) - Y_s(\tau))} \frac{\partial F}{\partial \eta} \\
& = \frac{1}{(Y_1(\tau) - Y_s(\tau))^2} \frac{\partial^2 F}{\partial \eta^2} - \frac{R}{St} \left(\frac{\partial \chi}{\partial \tau} + \eta_\tau \frac{\partial \chi}{\partial \eta} \right), \tag{5.86}
\end{aligned}$$

$$\begin{aligned}
& \frac{\partial}{\partial \tau} (\chi C_1) + \eta_\tau \frac{\partial}{\partial \eta} (\chi C_1) - k_0 R C_1 \left(\frac{\partial \chi}{\partial \tau} + \eta_\tau \frac{\partial \chi}{\partial \eta} \right) + \beta R (1 - \chi) k_0 \left(\frac{\partial C_1}{\partial \tau} + \eta_\tau \frac{\partial C_1}{\partial \eta} \right) \\
& + \frac{1}{\tau^{1/2} (Y_1(\tau) - Y_s(\tau))} \frac{\partial}{\partial \eta} (C_1 \tilde{U}) = 0, \tag{5.87}
\end{aligned}$$

$$F = \theta_m - \tilde{m} C_1, \tag{5.88}$$

where

$$\eta_\tau = - \left\{ \frac{\dot{Y}_s(\tau) + (\eta - 1) (\dot{Y}_1(\tau) - \dot{Y}_s(\tau))}{(Y_1(\tau) - Y_s(\tau))} \right\},$$

with dots denoting differentiation with respect to τ ; for $2 \leq \eta < 3$,

$$\frac{\partial \tilde{U}}{\partial \eta} = 0, \tag{5.89}$$

$$\begin{aligned}
& (Y_\infty(\tau) - Y_1(\tau))^2 \frac{\partial F}{\partial \tau} - \{ \dot{Y}_1(\tau) + (\eta - 2) (\dot{Y}_\infty(\tau) - \dot{Y}_1(\tau)) \} (Y_\infty(\tau) - Y_1(\tau)) \frac{\partial F}{\partial \eta} \\
& + \frac{(Y_\infty(\tau) - Y_1(\tau))}{\tau^{1/2}} \tilde{U} \frac{\partial F}{\partial \eta} = \frac{\partial^2 F}{\partial \eta^2}, \tag{5.90}
\end{aligned}$$

$$(Y_\infty(\tau) - Y_1(\tau)) \frac{\partial C_1}{\partial \tau} + \left(\frac{\tilde{U}}{\tau^{1/2}} - \{ \dot{Y}_1(\tau) + (\eta - 2) (\dot{Y}_\infty(\tau) - \dot{Y}_1(\tau)) \} \right) \frac{\partial C_1}{\partial \eta} = 0. \tag{5.91}$$

The boundary conditions are: at $\eta = 0$,

$$F = 0; \tag{5.92}$$

at $\eta = 1$,

$$\begin{cases} \chi = 0, & F = \theta_m - \tilde{m} C_1 & \text{if } C_1 < C_{\text{eut}} \\ F = \theta_{\text{eut}} & & \text{if } C_1 = C_{\text{eut}} \end{cases}, \tag{5.93}$$

$$\frac{1}{Y_1(\tau) - Y_s(\tau)} \left(\frac{\partial F}{\partial \eta} \right)_+ - \frac{1}{Y_s(\tau)} \left(\frac{\partial F}{\partial \eta} \right)_- = - \frac{\chi_s}{St} \dot{Y}_s(\tau), \tag{5.94}$$

$$\tilde{U} = (1 - R) \chi_s \tau^{1/2} \dot{Y}_s(\tau); \tag{5.95}$$

at $\eta = 2$,

$$F = \theta_m - \tilde{m} C_1, \tag{5.96}$$

$$\frac{1}{Y_\infty(\tau) - Y_1(\tau)} \left(\frac{\partial F}{\partial \eta} \right)_+ - \frac{1}{Y_1(\tau) - Y_s(\tau)} \left(\frac{\partial F}{\partial \eta} \right)_- = 0, \tag{5.97}$$

$$\chi = 1; \tag{5.98}$$

at $\eta = 3$,

$$\frac{\partial F}{\partial \eta} = 0, \quad (5.99)$$

$$\frac{\partial C_1}{\partial \eta} = 0. \quad (5.100)$$

As for the initial conditions, for $0 < \eta \leq 3$,

$$F = 1, \quad (5.101)$$

$$C_1 = C_0, \quad (5.102)$$

as well as

$$Y_l(0) = 0, \quad (5.103)$$

$$Y_s(0) = 0, \quad (5.104)$$

$$Y_\infty(0) = 1. \quad (5.105)$$

5.3.2 The limit as $\tau \rightarrow 0$

Let's now consider these equations in the limit as $\tau \rightarrow 0$. One will have that $Y_l, Y_s \rightarrow 0$ as $\tau \rightarrow 0$, and it is plausible to suppose that $Y_l, Y_s \sim \tau^{1/2}$. Let's therefore set

$$Y_l \sim \eta_{\text{liq}} \tau^{1/2}, \quad Y_s \sim \eta_{\text{sol}} \tau^{1/2}, \quad (5.106)$$

where η_{liq} and η_{sol} are to be determined. In order to obtain the position of the interface Y_∞ , one must recall the nondimensional form of the conservation of mass

$$\int_0^{Y_\infty(0)} dY = R \int_0^{Y_s(\tau)} dY + \int_{Y_s(\tau)}^{Y_l(\tau)} (\chi(1-R) + R) dY + \int_{Y_l(\tau)}^{Y_\infty(\tau)} dY, \quad (5.107)$$

using $Y_\infty(0) = 1$ and eq. (5.106) we obtain

$$Y_\infty \sim 1 + \tau^{1/2}(1-R) \left[\eta_{\text{liq}} - (\eta_{\text{liq}} - \eta_{\text{sol}}) \int_1^2 \chi d\eta \right]. \quad (5.108)$$

Previous experience in the solution of Stefan problems for which the domain of interest initially has zero thickness (MITCHELL; VYNNYCKY, 2009; MITCHELL; VYNNYCKY, 2014; MITCHELL; VYNNYCKY, 2016) indicates that, as $\tau \rightarrow 0$, a system of ordinary differential equations should be obtained. In this case, with primes denoting differentiation with respect to η , we arrive at: for $0 \leq \eta \leq 1$,

$$-\frac{1}{2} R \eta_{\text{sol}}^2 \eta F' = F''; \quad (5.109)$$

for $1 \leq \eta \leq 2$,

$$-\frac{1}{2} (1-R) \{ (2-\eta) \eta_{\text{sol}} + (\eta-1) \eta_{\text{liq}} \} \chi' + \tilde{U}' = 0, \quad (5.110)$$

$$\begin{aligned}
& (\eta_{\text{liq}} - \eta_{\text{sol}}) \left[\tilde{U} - \frac{1}{2} [\chi + (1 - \chi)R] \{ (2 - \eta) \eta_{\text{sol}} + (\eta - 1) \eta_{\text{liq}} \} \right] F' \\
& = F'' + \frac{1}{2} \frac{R}{St} (\eta_{\text{liq}} - \eta_{\text{sol}}) \{ (2 - \eta) \eta_{\text{sol}} + (\eta - 1) \eta_{\text{liq}} \} \chi', \tag{5.111}
\end{aligned}$$

$$\frac{1}{2} \{ (2 - \eta) \eta_{\text{sol}} + (\eta - 1) \eta_{\text{liq}} \} [k_0 R C_1 \chi' - (\chi C_1)' - \beta R (1 - \chi) k_0 C_1'] + (C_1 \tilde{U})' = 0 \tag{5.112}$$

$$F = \theta_m - \tilde{m} C_1; \tag{5.113}$$

for $2 \leq \eta < 3$,

$$\tilde{U}' = 0, \tag{5.114}$$

$$F' = 0, \tag{5.115}$$

$$C_1' = 0. \tag{5.116}$$

The boundary conditions are: at $\eta = 0$,

$$F = 0; \tag{5.117}$$

at $\eta = 1$,

$$\begin{cases} \chi = 0, & F = \theta_m - \tilde{m} C_1 & \text{if } C_1 < C_{\text{eut}} \\ F = \theta_{\text{eut}} & & \text{if } C_1 = C_{\text{eut}} \end{cases}, \tag{5.118}$$

$$\frac{(F')_+}{\eta_{\text{liq}} - \eta_{\text{sol}}} - \frac{(F')_-}{\eta_{\text{sol}}} = -\frac{\chi_s \eta_{\text{sol}}}{2St}, \tag{5.119}$$

$$\tilde{U} = \frac{1}{2} (1 - R) \chi_s \eta_{\text{sol}}; \tag{5.120}$$

at $\eta = 2$,

$$F = \theta_m - \tilde{m} C_1, \tag{5.121}$$

$$(F')_- = 0, \tag{5.122}$$

$$\chi = 1; \tag{5.123}$$

at $\eta = 3$,

$$F' = 0, \tag{5.124}$$

$$C_1' = 0. \tag{5.125}$$

There is now clearly a problem for $2 \leq \eta \leq 3$ since (5.115), subject to (5.101) and (5.124), implies that $F \equiv 1$, which contradicts (5.121). This is not surprising, since the second

derivative in η in (5.90) was neglected; in order for it to be retained, a boundary layer would be needed for which $\eta - 2 \sim \tau^{1/2}$, and so a further transformation has to be used,

$$\hat{\eta} = \frac{\eta - 2}{\tau^{1/2}}, \quad \mathcal{F} = F, \quad (5.126)$$

so that (5.90) becomes

$$(Y_\infty(\tau) - Y_1(\tau))^2 \left(\tau \frac{\partial \mathcal{F}}{\partial \tau} - \frac{1}{2} \hat{\eta} \frac{\partial \mathcal{F}}{\partial \hat{\eta}} \right) + \left\{ \tilde{U} - \tau^{1/2} \left\{ \dot{Y}_1(\tau) + \hat{\eta} \tau^{1/2} (\dot{Y}_\infty(\tau) - \dot{Y}_1(\tau)) \right\} \right\} \quad (5.127)$$

$$(Y_\infty(\tau) - Y_1(\tau)) \frac{\partial \mathcal{F}}{\partial \hat{\eta}} = \frac{\partial^2 \mathcal{F}}{\partial \hat{\eta}^2}, \quad (5.128)$$

leading to, as $\tau \rightarrow 0$,

$$Y_\infty(0) \left(\tilde{U} - \frac{1}{2} Y_\infty(0) \hat{\eta} - \frac{1}{2} \eta_{\text{liq}} \right) \frac{d\mathcal{F}}{d\hat{\eta}} = \frac{d^2 \mathcal{F}}{d\hat{\eta}^2}, \quad (5.129)$$

where $\mathcal{F}$ satisfies

$$\mathcal{F} = \theta_m - \tilde{m}C_l \quad \text{at } \hat{\eta} = 0, \quad (5.130)$$

$$\mathcal{F} \rightarrow 1 \quad \text{as } \hat{\eta} \rightarrow \infty. \quad (5.131)$$

Also, (5.97) now becomes, instead of (5.122),

$$\frac{(\mathcal{F}')_{\hat{\eta}=0}}{Y_\infty(0)} = \frac{(F')_{\eta=2-}}{\eta_{\text{liq}} - \eta_{\text{sol}}}. \quad (5.132)$$

For $0 \leq \eta \leq 1$, there is an analytical solution in the form

$$F = \frac{\theta_s \operatorname{erf}\left(\frac{R^{1/2}\eta}{2}\right)}{\operatorname{erf}\left(\frac{R^{1/2}\eta_{\text{sol}}}{2}\right)}, \quad (5.133)$$

where $\theta_s = (F)_{\eta=1}$; thus, θ_s must itself be iterated via (5.118). To obtain the solution to (5.129)-(5.131), let's set

$$\bar{\eta} = (Y_\infty(0) \hat{\eta} + \eta_{\text{liq}} - 2\tilde{U}) / Y_\infty^{1/2}(0), \quad (5.134)$$

leading to

$$-\frac{1}{2} \bar{\eta} \mathcal{F}' = \mathcal{F}'', \quad (5.135)$$

subject to

$$\mathcal{F} = \theta_m - \tilde{m}C_l \quad \text{at } \bar{\eta} = (\eta_{\text{liq}} - 2\tilde{U}) / Y_\infty^{1/2}(0), \quad (5.136)$$

$$\mathcal{F} \rightarrow 1 \quad \text{as } \bar{\eta} \rightarrow \infty. \quad (5.137)$$

Figure 5.3 – Schematic of the solution structure for small τ in the η -space. The dashed line indicates a boundary layer in θ of width $\tau^{1/2}$, with $\eta - 2 \sim \tau^{1/2}$.

Now,

$$\mathcal{F} = A \operatorname{erf}\left(\frac{\tilde{\eta}}{2}\right) + B, \quad (5.138)$$

where

$$A = \frac{1 - \theta_{\text{liq}}}{1 - \operatorname{erf}\left(\frac{\eta_{\text{liq}} - 2\tilde{U}}{2Y_{\infty}^{1/2}(0)}\right)}, \quad B = \frac{\theta_{\text{liq}} - \operatorname{erf}\left(\frac{\eta_{\text{liq}} - 2\tilde{U}}{2Y_{\infty}^{1/2}(0)}\right)}{1 - \operatorname{erf}\left(\frac{\eta_{\text{liq}} - 2\tilde{U}}{2Y_{\infty}^{1/2}(0)}\right)}, \quad (5.139)$$

where $\theta_{\text{liq}} = \theta_m - \tilde{m}C_0$. Note that the latter comes from (5.116) and (5.125), which both imply that $C_1 = C_0$ at $\eta = 2$. Also, observe that, although there is a boundary layer for F at $\eta = 2$ as $\tau \rightarrow 0$, there is no boundary layer for C_1 .

A schematic of the solution structure for small τ in the η -space is given in Fig. 5.3, showing the aforementioned boundary layer that was firstly reported in the literature by (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020). It must be noticed that the set of Landau transformations described in the beginning of Section 5.3.1 is essential for the analysis leading to this finding. In fact, analogous investigation would reveal the same feature in the solution structure for the problem of a solidifying sphere considered in (MCCUE; WU; HILL, 2008), although it went unnoticed by the authors. The additional investigation for a solidifying sphere is conducted in the Appendix of (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

5.4 Numerical Implementation

The numerical results presented in the next Section 5.5 are obtained by solving the mathematical models formulated in Section 5.2 using a finite elements method (FEM) implemented by the commercial software COMSOL Multiphysics.

The finite elements method approximates the solution u for each dependent variables in the system of differential equations (temperatures, liquid fraction, velocity and concentration) by a function u_h written as a linear combination of basis functions according to the expressions:

$$u \sim u_h, \quad (5.140)$$

$$u_h = \sum_i u_i \phi_i, \quad (5.141)$$

where ϕ_i denotes the basis functions and u_i denotes the coefficients of the functions that approximate u with u_h . The FEM offers the possibility to choose among a vast selection of basis functions, many of which are programmed into the COMSOL software. The results presented in the following sections were obtained using quadratic Lagrangian functions. The moving domain boundaries are handled by the ALE method with Winslow smoothing. The time discretization is carried out using a second-order backwards differentiation formula (BDF), with a backward Euler formula as initialization, while the resulting nonlinear system is solved by Newton method that iterates until the specified relative tolerance exceeds the weighted Euclidian norm of the residual. The relative tolerance for the results presented next is 1×10^{-3} , unless otherwise specified.

The method seems appropriate for the solution of the time-dependent problem since the dependent variables profiles are not expected to have any sharp gradients. According to (COMSOL, 2018), the time step is accepted if

$$\left(\frac{1}{M} \sum_j \frac{1}{N_j} \sum_i \left(\frac{|E_{U_i}|}{A_{s,i} + R|U_i|} \right)^2 \right)^{1/2} < 1 \quad (5.142)$$

where E_U is the solver's estimate of the absolute error in Y , $A_{s,i}$ is the scaled absolute tolerance for the degree of freedom i , M is the number of fields, R is the relative tolerance, N_j is the number of degrees of freedom in the field j , and U_i is the scaled solution vector. The number of fields means the quantity of dependent variables in the PDE system and the degree of freedom is given by the number of elements in the computational domain times the order of the Lagrangian shape function. The scaling is done according to the initial values for each variable, the relative tolerance is informed as an input to the time-dependent solver, while the absolute tolerance is computed from the input values A_k :

$$A_{s,i} = A_k(\Omega + ||U||_{2,i}), \quad \text{where} \quad \Omega = \begin{cases} (1 - e^{-\alpha j})||U||_{\infty,k_i} + e^{-\alpha j}, & 0 < ||U||_{\infty,k_i} < 1 \\ 1, & \text{else} \end{cases}, \quad (5.143)$$

where $\alpha = 0.2$, j is the time-step iteration number and $\|\cdot\|_2$, $\|\cdot\|_\infty$ are the 2-norm and maximum norm, respectively, for each dependent variable k_i . Where A_{k_i} is the input value A_k for the field k and DOF i . As a result, the absolute tolerance is updated at each time-step iteration.

A report was generated using the software interface and made available through the links in the Appendix A - for the small-time similar problem, Appendix B - for the three-regions non-similar problem, and Appendix C - for the two-regions non-similar problem. These files provide a way of documenting the simulations setups, distributing information about their programming and facilitating the reproduction of results by the interested reader.

5.5 Results

Here, the Section 5.5.1 is focused on analytical results that can be extracted when $R = 1$, before moving on to give solutions for $R \neq 1$ in section 5.5.2; the focus here is on the similarity solution for small times. Section 5.5.3 presents the numerical results for the full non-similar problem, while Section 5.5.4 carries out a validation for the similar and non-similar solutions.

5.5.1 $R = 1$ and $\tau \rightarrow 0$

In this case, equation (5.62), with the assistance of (5.60), reduces to

$$\frac{\partial}{\partial \tau} (\chi C_1) - k_0 C_1 \frac{\partial \chi}{\partial \tau} + \beta (1 - \chi) k_0 \frac{\partial C_1}{\partial \tau} = 0; \quad (5.144)$$

which can be written as

$$\chi \frac{\partial C_1}{\partial \tau} \frac{\partial \chi}{\partial \tau} + C_1 \frac{\partial \chi}{\partial \tau} - k_0 C_1 \frac{\partial \chi}{\partial \tau} + \beta (1 - \chi) k_0 \frac{\partial C_1}{\partial \tau} \frac{\partial \chi}{\partial \tau} = 0 \quad (5.145)$$

thus

$$(\chi + \beta(1 - \chi)k_0) \frac{\partial C_1}{\partial \chi} = C_1(k_0 - 1) \quad (5.146)$$

this can be integrated exactly to give

$$\log C_1 = \log \left\{ \alpha (\chi + \beta k_0 (1 - \chi))^{\frac{k_0 - 1}{1 - \beta k_0}} \right\} \quad (5.147)$$

where α is the constant of integration that must be defined by using the a boundary condition. Here we can use the fact that $C_1 = C_0$ when $\chi = 1$, to obtain

$$C_1 = C_0 (\chi + \beta k_0 (1 - \chi))^{\frac{k_0 - 1}{1 - \beta k_0}}. \quad (5.148)$$

The next question concerns what should be the value of χ_s , i.e. χ at $Y = Y_s(\tau)$. For example, if $\chi_s = 0$, we must have

$$C_1 = C_0 (\beta k_0)^{\frac{k_0 - 1}{1 - \beta k_0}}$$

Figure 5.4 – The curve in (β, C_0) -space which determines whether $\chi_s = 0$ or $\chi_s > 0$ ($R = 1$)

there, and therefore we would need

$$C_0 (\beta k_0)^{\frac{k_0 - 1}{1 - \beta k_0}} < C_{\text{eut}}; \quad (5.149)$$

otherwise, we have $\chi_s > 0$. An expression for χ_s valid for both cases is then

$$\chi_s = \max \left(0, \frac{1}{1 - \beta k_0} \left\{ \left(\frac{C_0}{C_{\text{eut}}} \right)^{\frac{1 - \beta k_0}{1 - k_0}} - \beta k_0 \right\} \right). \quad (5.150)$$

Fig. 5.4 shows the curve in (β, C_0) -space, based on (5.149), which delineates whether $\chi_s = 0$ or $\chi_s > 0$; thus, as β decreases, the range of values of C_0 for which eutectic solidification occurs, i.e. $\chi_s > 0$, increases. On the other hand, Fig. 5.5 shows χ_s as a function of β , as given in equation (5.150), for three different values of C_0 . Of significance here is the fact that $\chi_s = 0$ for $\beta \gtrsim 0.8$ for the lowest value of C_0 given. Hence, for values of β lower than this, eutectic solidification would occur. Moreover, for eutectic solidification to occur for the whole range of β , we would need $k_0 C_{\text{eut}} < C_0 \leq C_{\text{eut}}$, as would be obtained by requiring $\chi_s > 0$ for $\beta = 1$ in equation (5.150).

5.5.2 $R \neq 1$ and $\tau \rightarrow 0$

In this case, one does not have equation (5.148) for guidance, and consequently there is no closed-form expression for χ_s , which must instead be computed numerically as part of the solution. Neither it is known *a priori* at what value of β the transition from non-eutectic to eutectic solidification would occur. Therefore, the information must be obtained as part of the

Figure 5.5 – χ_s as a function of β for three values of C_0 ($R = 1$)

solution and the ability to do so allow us to build a transition curve similar to the one observed in Fig. 5.4 for a range of parameters.

Next, the transition curve is presented for different values of density ratio R , cooling boundary temperature T_w , and superheat δT , as a means of understanding how each of these parameters affect the nature of the solidification process. The effect of the density ratio R is presented in Fig. 5.6, where the curve moves downwards as the value of R increases, the slight difference indicates that the value of β at which the transition occurs increases with R .

Fig. 5.7 shows the curve in (β, C_0) -space for different values of superheat. Note that $\delta T = 26.7\text{K}$ corresponds to the curve in Fig. 5.6 with $R = 1.3$. Fig. 5.8 shows the same curve for different cooling surface temperatures, where $T_w = 621\text{K}$ compares to the data in Fig. 5.6. It must be pointed out that while the solution was obtained for the non-dimensional model, the descriptive labels are displayed in dimensional terms, to provide a more intelligible physical meaning.

In both cases, the curves are indistinguishably on top of each other, showing that changing the cooling surface temperature and superheat within the tested range has no effect on the transition curve for the limit $\tau \rightarrow 0$. Even so, the importance of the cooling temperature and superheat for the solute concentration profile can not be ruled out for $\tau > 0$ and its effects will be addressed again in Section 5.5.3.

In what follows, let's consider the temperature, liquid fraction, velocity and position of solid-mush and mush-liquid interfaces for small τ in the limit as $\tau \rightarrow 0$ – and later carry out the treatment for $\tau > 0$. Results are given below for $C_0 = 5\%$ wt Cu and $R = 1, 1.1, 1.2, 1.3$;

Figure 5.6 – The curve in (β, C_0) -space for different values of R .

Figure 5.7 – The curve in (β, C_0) -space for $R = 1.3$ and different values of superheat δT .

Figure 5.8 – The curve in (β, C_0) -space for $R = 1.3$ and different cooling surface temperatures T_w .

Figure 5.9 – θ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (AS-SUNÇÃO; VYNNYCKY; MITCHELL, 2020).

$T_w = 721\text{K}, 621\text{K}, 521\text{K}$; $\delta T = 100\text{K}, 26.7\text{K}, 1\text{K}$; the value of C_0 is the same as that used in (VOLLER, 1997), although a key difference is that these results are only for the limit as $\tau \rightarrow 0$, and will be different for $\tau > 0$, since there is no similarity solution that is valid for all time.

Figs. 5.9(a) and (b) show θ as a function of η ($1 \leq \eta \leq 2$) for four values of R when $\beta = 0$ and $\beta = 1$, respectively. The curves in Fig. 5.9(a) appear to lie on top of each other, which is a consequence of the fact that $\theta = \theta_{\text{eut}}$ at $\eta = 1$ and $\theta = \theta_m - \tilde{m}C_0$ at $\eta = 2$ for all of them. In Fig. 5.9(b), on the other hand, $\theta > \theta_{\text{eut}}$ at $\eta = 1$, and there is some variation, with θ at $\eta = 1$ decreasing as R increases.

Figs. 5.10(a) and (b) show χ as a function of η for the same four values of R when $\beta = 0$

Figure 5.10 – χ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

Figure 5.11 – χ as a function of η for three values of δT and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$.

Figure 5.12 – χ as a function of η for three values of cooling boundary temperature T_w and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$.

Figure 5.13 – $\tilde{U}$ as a function of η for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$. As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

Figure 5.14 – $\tilde{U}$ as a function of η for three values of superheat δT and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$.

and $\beta = 1$, respectively. In both plots, the value of χ at $\eta = 1$ for $R = 1$ corresponds to the values for χ_s shown in Fig. 5.5; however, for $\beta = 0$, the value of χ_s increases with R , but remains zero for $\beta = 1$, indicating that $C_1 < C_{\text{cut}}$ for all four curves in this plot.

Figs. 5.11(a) and (b) show χ as a function of η for $R = 1.3$, and superheat $\delta T = 100\text{K}, 26.7\text{K}, 1\text{K}$, when $\beta = 0$ and $\beta = 1$, respectively. The value of χ_s remains unchanged for all the curves, however $\frac{\partial \chi}{\partial \eta} \rightarrow 0$ at $\eta = 2$ as the superheat decreases, at the same time as the average value of χ increases.

Figs. 5.12(a) and (b) show χ as a function of η for $R = 1.3$, and cooling boundary temperature $T_W = 721\text{K}, 621\text{K}, 521\text{K}$, when $\beta = 0$ and $\beta = 1$, respectively. We can observe that changing the cooling temperature within this range has little to no effect on the liquid fraction profile.

Figs. 5.13(a) and (b) show $\tilde{U}$ as a function of η for four values of R when $\beta = 0$ and $\beta = 1$, respectively. Here, the profiles change significantly with respect to R , although less so

Figure 5.15 – $\tilde{U}$ as a function of η for three values of cooling boundary temperature T_w and $R = 1.3$ for: (a) $\beta = 0$; (b) $\beta = 1$.

with respect to β . In particular, the values of $\tilde{U}$ at $\eta = 2$ are almost identical for $\beta = 0$ and $\beta = 1$, but are equal to zero at $\eta = 1$ for the latter; this is because $\chi_s = 0$.

Figs. 5.14(a) and (b) show $\tilde{U}$ as a function of η for three values of δT when $\beta = 0$ and $\beta = 1$, respectively. It can be observed that the absolute value of velocity increases as the superheat decreases, this behaviour can be justified in two steps: first we observe that the superheat is directly proportional to the amount of heat that must be removed from the liquid region in order to turn it into mush; secondly, we must recall from eq. (5.49) that $(U)_{y_l(t)} = \dot{y}_\infty(t)$. Thus, it may be expected that a smaller superheat would lead to a quicker solidification process, hence higher velocity $\dot{y}_\infty$ could be attained and, consequently, greater values for $\tilde{U}$.

Figs. 5.15(a) and (b) show $\tilde{U}$ as a function of η for three values of T_w when $\beta = 0$ and $\beta = 1$, respectively. The effect of the cooling temperature on the $\tilde{U}$ profiles, as observed in the results, can be justified with a similar argument: the lower temperature at the cooling surface would lead to a quicker solidification, where the interfaces move faster and forces the liquid portion to move at higher velocity towards the solid/mush interface in order to compensate for the density changes.

Figs. 5.16(a) and (b) show η_{sol} and η_{liq} as functions of β for the same four values of R . Most distinct here are the kinks in Fig. 5.16(a) for β just in excess of 0.8. Whereas these might be expected for the $R = 1$ curves, in view of the earlier discussion in section 5.5.1, the kinks for the other curves indicate that a similar transition from non-eutectic to eutectic solidification occurs; in fact, further computations for more values of β in the interval $0.8 \leq \beta \leq 0.85$ indicated that the critical value of β for the transition increased as R was increased. On the other hand, no kinks are visible in Fig. 5.16(b) although, most likely, it is the case that the kinks are extremely mild in this case - a reflection of the fact that their cause is at the solid boundary, rather than at the liquid boundary.

Figs. 5.17(a) and (b) show η_{sol} and η_{liq} as functions of β for three different values of

Figure 5.16 – η_{sol} (a) and η_{liq} (b) as functions of β for four values of R . As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

Figure 5.17 – η_{sol} (a) and η_{liq} (b) as functions of β with $R = 1.3$ for different values of superheat δT .

Figure 5.18 – η_{sol} (a) and η_{liq} (b) as functions of β with $R = 1.3$ for different temperatures of cooling boundary T_w .

Figure 5.19 – The solute concentration in the solid, C_{solid} , as a function of β for four values of R . As presented in (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

δT . The line corresponding to $\delta T = 26.7\text{K}$ compares to the results presented in Figs. 5.16(a) and (b) for $R = 1.3$. The location of both interfaces η_{sol} and η_{liq} reveals that the thickness of the mushy region (given by $\eta_{\text{liq}} - \eta_{\text{sol}}$) increases with the superheat and that both interfaces move faster as the superheat decreases.

Figs. 5.18(a) and (b) show η_{sol} and η_{liq} as functions of β for three different of T_w . Here, the lower temperature at the cooling boundary leads to a quicker solidification process, with the interfaces traveling faster towards the rightmost boundary for small values of τ .

Finally, we note that although computations have been so far carried out only in the limit as $\tau \rightarrow 0$, it is nevertheless possible to demonstrate the well-known phenomenon of inverse segregation, whereby the solute concentration is higher at the cooling surface. Fig. 5.19 shows the solute concentration in the fully solidified region, which shall be denoted by C_{solid} , as a function of β for four values of R ; note that in general $C_{\text{solid}} \neq C_s|_{\eta=1}$, but must be computed from (5.28) as

$$\rho_s C_{\text{solid}} = \chi_s \rho_l C_l|_{\eta=1} + \rho_s \int_0^{1-\chi_s} \left(C_s + \beta \chi' \frac{dC_s}{d\chi'} \right) d\chi'. \quad (5.151)$$

From the figure, it is evident that $C_{\text{solid}} > C_0$ for $R > 1$, but that $C_{\text{solid}} = C_0$ for $R = 1$, as would be expected; in addition, kinks are just about visible in the curves for which $R > 1$, for the reasons discussed in the previous paragraph, although these are much milder than in Fig. 5.16(a).

5.5.3 Non-similar problem: $\tau > 0$

The full non-similar problem is valid from τ_0 until the end of the solidification process, which is characterized by the complete depletion of mush region that occurs at the moment τ_m .

The problem is defined by a transient model and solved for the solid, mush and liquid regions until the moment there is no molten material left in the liquid region, here labeled τ_l , from this point the temperature, liquid fraction, and velocity profiles, as well as the interfaces locations are used as initial values for the two-regions transient model that accounts for the solid and mush regions only. The set of equations, boundary conditions and initial values are summarized in Table 9.

		Solid	Mush	Liquid
Three regions	G.E.	eq. (5.59)	eqs. (5.60–5.63)	eqs. (5.64–5.66)
	B.C.	eq. (5.67), eq. (5.68)	eq. (5.69), eq. (5.70)	eqs. (5.73–5.75)
	I.V.	eq. (5.133)	Figs. 5.9–5.16	eq. (5.138)
Two regions	G.E.	eq. (5.59)	eqs. (5.60–5.63)	
	B.C.	eq. (5.67), eq. (5.68)	eq. (5.69), eq. (5.70), eq. (5.74)	
	I.V.	Fig. 5.20	Figs. 5.21–5.23	

Table 9 – Mathematical models valid for three or two-regions formulations, defined by Governing Equations (G.E.), Boundary and Interfacial Conditions (B.C.), and Initial Values (I.V.).

The set of equations solved for the non-similar problem corresponds to the formulation obtained by nondimensionalization presented in Section 5.2, prior to the interface immobilization obtained through the Landau transformation carried out in Section 5.3. The remarkable advantage of the model with moving interfaces over the one posed in a fixed spatial domain lies in its predisposition to be extended to a two-dimensional formulation. Therefore, the work invested in solving the problem with moving boundaries can be perceived as an fundamental part of the efforts towards developing a more advanced formulation.

Figure 5.20 – $\theta(\tau)$ as a function of Y inside the solid region for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$

Figure 5.21 – $\theta(\tau_1)$ as a function of Y inside the mush region for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$

Figure 5.22 – $\chi(\tau_1)$ as a function of Y for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$

Figure 5.23 – $\hat{U}(\tau_1)$ as a function of Y for four values of R for: (a) $\beta = 0$; (b) $\beta = 1$

Next, let's analyze the results obtained for temperature, liquid fraction and velocity at the time the liquid region vanishes. Figs. 5.20(a) and 5.20(b) show θ at $\tau = \tau_1$ as a function of Y across the solid region ($0 \leq Y \leq Y_s$) for four values of R when $\beta = 0$ and $\beta = 1$, respectively. The curves in Fig. 5.20(a) and (b) show a temperature profile more or less linear increasing from the nondimensional wall temperature towards the temperature at the solid-mush interface, which is defined as θ_{eut} for eutectic solidification, or computed as part of the solution for a non-eutectic solidification. As it is going to be detailed later in this Section, the eutectic case is observed for $\beta = 0$, while the non-eutectic is occurring for $\beta = 1$. The difference in length noticed on the x-axis are explained by distinct trajectory of solid-mush interface when subject to different density ratios.

Curves in Figs. 5.21(a) and 5.21(b) show the temperature θ at the same time and values of R with $\beta = 0$ and $\beta = 1$, presented as a function of Y inside the mush region ($Y_s \leq Y \leq Y_1$). Here we can notice the temperature increasing towards θ_1 , which is the boundary condition valid for this configuration. At the solid-mush interface the curves in Fig. 5.21(a) display the same value of θ . In Fig. 5.21(b), on the other hand, shows divergent values at the same interface, implying that this quantity depends inversely on the density ratio indicating again a non-eutectic behaviour that is more likely to turn eutectic for greater values of R .

Figs. 5.22(a) and 5.22(b) show χ as a function of Y for the same four values of R and β . In both figures, the liquid fraction increases across the mush region reaching $\chi = 1$ at the mush-liquid interface. Figs. 5.23(a)–5.23(b) represent the liquid phase velocity developed inside the mush region. In both plots this quantity is zero for $R = 1$, as there is no movement due to density differences. When $R > 1$ the negative velocity indicates the liquid phase moving from the bulk towards the casting wall, the absolute velocity at the solid-mush interface increases with R for $\beta = 0$, but is kept as zero at this position for $\beta = 1$.

As previously described, one of the main features of this model is the interface tracking that allows us to compute the limits between the solid and mushy regions: Y_s and Y_1 , plus the location of the rightmost boundary Y_∞ . The initial computational domain is given by eq. (5.106–5.108), using the values for η_{sol} , η_{liq} , and liquid fraction profile obtained as the small-time solution, leading to the configuration shown in Table 10.

R	Scheil			lever rule		
	$Y_s^{\tau_0}$	$Y_1^{\tau_0}$	$Y_\infty^{\tau_0}$	$Y_s^{\tau_0}$	$Y_1^{\tau_0}$	$Y_\infty^{\tau_0}$
1.0	2.0579e-2	3.4449e-2	1.0000	2.1910e-2	3.3911e-2	1.0000
1.1	1.9757e-2	3.3123e-2	9.9714e-1	2.0874e-2	3.2543e-2	9.9710e-1
1.2	1.9031e-2	3.1948e-2	9.9450e-1	1.9971e-2	3.1335e-2	9.9444e-1
1.3	1.8382e-2	3.0896e-2	9.9920e-1	1.9174e-2	3.0258e-2	9.9197e-1

Table 10 – Initial domain configuration for $\tau > 0$.

Using those values as initial interface positions, the Figs. 5.24–5.25 display the movement of the interfaces during the solidification process that takes place from the initial time τ_0 until

Figure 5.24 – Positions of solid-mush, mush-liquid, and liquid interfaces with $\beta = 0$ for different density ratios: (a) $R = 1.0$; (b) $R = 1.1$; (c) $R = 1.2$; (d) $R = 1.3$

the material is fully solidified, for two extreme values on the interval $0 \leq \beta \leq 1$. The rightmost boundary remains fixed at its initial value for $R = 1.0$, as it should be expected. For $R > 1.0$, its value start to decrease towards $1/R$ preserving the mass balance throughout the process, this movement can be seen as the shrinkage expected on any material with density ratio greater than 1.0.

Two important events occur at the intersection of lines Y_∞ and Y_l , Y_s and Y_l , that represent, respectively, the approximate times and locations at which the liquid and the mush regions disappear. These values are listed in Tables 11-12, according to which it is possible to note that a higher density ratio leads to a shorter solidification time. Moreover, one can also observe that the different assumptions regarding solute transport at the microscale (Scheil or lever rule) could not significantly affect neither the velocity of the solid-mush and mush-liquid interfaces nor the time it takes for any of the regions to vanish.

Fig. 5.26 shows the final solute concentration C_{solid} across the solidified domain according to eq. (5.28), with $\beta = 0$ and $c_0 = 5\text{wt\%}$. In the portion adjacent to the cast, the calculated concentration is above the initial value and more or less constant. It should be highlighted that

Figure 5.25 – Positions of solid-mush, mush-liquid, and liquid interfaces with $\beta = 1$ for different density ratios: (a) $R = 1.0$; (b) $R = 1.1$; (c) $R = 1.2$; (d) $R = 1.3$

R	τ_l	Y_l^{final}	τ_m	Y_m^{final}	$1/R$
1.0	3.9950e-01	9.9996e-01	9.3472e-01	1.00	1.0000e-01
1.1	4.6650e-01	9.2920e-01	8.5752e-01	9.0819e-01	9.0909e-01
1.2	4.4168e-01	8.6796e-01	7.8902e-01	8.3058e-01	8.3333e-01
1.3	4.1701e-01	8.1481e-01	7.2844e-01	7.6438e-01	7.6923e-01

Table 11 – Considering $\beta = 0$, τ_l and τ_m are respectively the time it takes for the liquid and mush regions to vanish, while $Y_l^{\text{final}} = Y_\infty(\tau_l)$ and $Y_m^{\text{final}} = Y_s(\tau_m)$.

this solidified region with homogeneous concentration is formed while the liquid region still occupies a significant portion of the material, decreasing thereafter. This behavioral change coincides with the replacement of the boundary condition at the end of mush region (Y_l) from $\theta_m = \theta_l$ to $\theta' = 0$. The second half of the solidified material, in turn, is characterized by a lower solute concentration.

The variations on solute concentration around the c_0 , which identify the undesired macrosegregation defect, could have its occurrence summarized by the standard deviation calculated from a given concentration profile as $\alpha = \sqrt{\frac{(c_{0,i} - c_{\text{solid},i})^2}{N}}$, where N is the number of

Figure 5.26 – Final solute concentration across solidified domain with $\beta = 0$. Figure 5.27 – Final solute concentration across solidified domain with $\beta = 1$.

R	τ_l	Y_l^{final}	τ_m	Y_m^{final}	$1/R$
1.0	4.0867e-01	9.9997e-01	8.7998e-01	9.9993e-01	1.0000e-00
1.1	4.9797e-01	9.2602e-01	8.2208e-01	9.0838e-01	9.0909e-01
1.2	4.5143e-01	8.6513e-01	7.6700e-01	8.3118e-01	8.3333e-01
1.3	4.3594e-01	8.0855e-01	7.0701e-01	7.6356e-01	7.6923e-01

Table 12 – Considering $\beta = 1$, τ_l and τ_m are respectively the time it takes for the liquid and mush regions to vanish, while $Y_l^{\text{final}} = Y_\infty(\tau_l)$ and $Y_m^{\text{final}} = Y_s(\tau_m)$.

Figure 5.28 – Final solute concentration across solidified domain for different values of superheat δT . Considering $\beta = 0$ and $R = 1.3$.

elements on the domain. These results are presented in Table 13, which correlates the increase in the density ratio to the severity of macrosegregation. It must be noted that the deviation obtained for $R=1.0$, which should be zero on an ideal result, could be related to numerical errors and has a considerable small order of magnitude.

R	Standard deviation on c_0	
	Scheil	lever rule
1.0	4.0737e-04	4.6610e-04
1.1	1.0786e-01	2.3392e-01
1.2	2.0981e-01	4.0228e-01
1.3	2.9856e-01	4.0182e-01

Table 13 – Standard deviation (α) calculated for each combination of parameters.

Fig. 5.28 shows the final solute concentration across the solidified domain for three values of δT , with $\beta = 0$, $R = 1.3$ and $c_0 = 5\text{wt}\%$. Here, $\delta T = 26.7\text{K}$ compares to Fig. 5.26 and

Figure 5.29 – Final solute concentration across solidified domain for different values of cooling surface temperature T_w . Considering $\beta = 0$ and $R = 1.3$.

it can be observed that the macrosegregation is slightly reduced as the superheat increases, which can be explained by the lower velocity magnitude as presented in Fig. 5.14.

Fig. 5.29 shows the final solute concentration across the solidified domain for three values of T_w , with $\beta = 0$, $R = 1.3$ and $c_0 = 5\text{wt}\%$. Looking back at $\tilde{U}$ profile presented in Fig. 5.15, note that increasing the cooling boundary temperature tends to decrease the velocity magnitude, therefore, one could expect that it would also result in a decrease of macrosegregation. However, what the comparison clearly shows is the opposite trend with lower temperatures leading to smaller macrosegregation.

In order to understand this behaviour we must look at the columns τ_l and τ_m in Table 14, where the first marks the disappearance of the liquid region, and the second indicates the end of the solidification process. We observe that increasing the cooling boundary temperature T_w by 100K leads to a process 56.14% slower, which favors the movement of solute inside the mushy region resulting in a more heterogeneous concentration profile.

Fig. 5.30 shows an attempt to minimize the macrosegregation by using a combination of higher superheat and lower cooling boundary temperature. According to Table 14, the standard deviation on the initial concentration c_0 is 15.50% smaller for $\delta T = 100\text{K}$, $T_w = 521\text{K}$, and 42.12% smaller for $\delta T = 200\text{K}$, $T_w = 421\text{K}$ when compared to the concentration profile obtained for $\delta T = 26.7\text{K}$, $T_w = 621\text{K}$.

Another important aspect of this approach lies on the choice of a constant τ_0 as the limiting value for the validity of the small-time solution, and established as the initial time

Figure 5.30 – Final solute concentration across solidified domain for different values of superheat δT and cooling surface temperature T_w . Considering $\beta = 0$ and $R = 1.3$.

Parameters		τ_l		τ_m		Std. deviation α	
δT [K]	T_w [K]	Measured	%	Measured	%	Measured	%
26.7	621	4.1701e-01	0.00	7.2844e-01	0.00	2.9856e-01	0.00
1.0	621	3.8349e-01	-8.04	7.0168e-01	-3.67	3.1520e-01	5.57
100.0	621	4.9081e-01	17.69	7.9139e-01	8.64	2.8473e-01	-4.63
26.7	721	5.2052e-01	24.82	1.1374e-00	56.14	3.8322e-01	2.83
26.7	521	3.5317e-01	-15.31	5.3676e-01	-26.31	2.7237e-01	-8.77
100.0	521	4.1228e-01	-1.13	6.0811e-01	-16.52	2.5228e-01	-15.50
200.0	421	4.1336e-01	-0.87	5.5120e-01	-24.33	1.7280e-01	-42.12

Table 14 – Non-dimensional times τ_l , τ_m necessary for the disappearance of liquid and mush regions, respectively; standard deviation (α) on c_0 calculated for different values of superheat δT and cooling boundary temperature T_w . Considering $\beta = 0$ and $R = 1.3$.

from which the transient model should be computed. The movement of solid-mush and mush-liquid interfaces, first assumed to behave like $Y_s \sim \eta_{\text{sol}} \tau^{1/2}$ and $Y_l \sim \eta_{\text{liq}} \tau^{1/2}$ are compared to the obtained profiles, i.e., the values computed for the interfaces from τ_0 to the end of the solidification process. From Fig. 5.31, it is clear that the first assumptions must not be valid at all times for a finite domain, and it is then desirable to chose a value for τ_0 that results in a sufficiently large initial solid and mush regions, yet does not degrade the quality of the numerical solution.

Figs. 5.32–5.33 illustrate the behavior of the solid-mush and mush-liquid interfaces, respectively, analyzing these results we are able to compare the profiles obtained for different values of τ_0 in the range of 1×10^{-4} to 5×10^{-2} . Here, it is evident that increasing the value

Figure 5.31 – Comparison between solid-mush and mush-liquid interfaces vs small-time assumptions.

Figure 5.32 – Position of the solid-mush interface Y_s vs τ for different values of τ_0 . Considering $\beta = 1$ and $R = 1.0$.

of τ_0 leads to a greater error summarized in Table 15, which is computed as the difference between the initial interfaces location for given τ_0 and the interface position on the reference curve corresponding to $\tau_0 = 1 \times 10^{-4}$ evaluated at the same time τ . These results justify the choice of $\tau_0 = 1 \times 10^{-3}$ as reasonable small initial time for the non-similar problem.

Considering the boundary conditions defined according to eq. (5.68), the solidification

Figure 5.33 – Position of the mush-liquid interface Y_l vs τ for different values of τ_0 . Considering $\beta = 1$ and $R = 1.0$.

τ_0	$\ Y_s^{\tau_0} - Y_s^*\ $	$\ Y_l^{\tau_0} - Y_l^*\ $
5e-4	1.1031e-03	3.0858e-03
1e-3	1.8188e-03	4.8336e-03
5e-3	4.4020e-03	1.1671e-02
1e-2	6.2914e-03	1.6692e-02
5e-2	1.4458e-02	3.8337e-02

Table 15 – Absolute error on initial solid-mush and mush-liquid interfaces, with the reference values $Y_s^* = Y_s(\tau_0 = 1e-4)$ and $Y_l^* = Y_l(\tau_0 = 1e-4)$. Considering $\beta = 1$ and $R = 1.0$.

process for the one-dimensional multi-domain model with finite geometry can be separated into three categories: purely non-eutectic; purely eutectic; or initially non-eutectic transitioning to eutectic solidification. As pointed out in Section 5.1.4.1, it is impossible to know beforehand whether the transition would occur, and that answer can only be obtained through numerical results.

In Table 16 these results are summarized for a set of parameters and, as it can be observed, when assuming $\beta = 0$, the process is entirely eutectic. If $\beta = 1$, on the other hand, the process may be non-eutectic throughout, or transition into the eutectic solidification after the solidification front reaches the length Y_{eut} , the location and time of this event depends on the density ratio, with a higher portion of eutectic solidification taking place for greater values of R .

Looking at this data together with the values presented in Table 12, we are able to compute the percentage of the final domain that was solidified under eutectic conditions, which is presented in Table 17. Once again we see that, for this combination of parameters, a higher

density ratio allows the process to become eutectic when applying the lever rule.

R	Scheil		lever rule	
	Type	Y_{eut}	Type	Y_{eut}
1.0	eutectic	–	non-eutectic	–
1.1	eutectic	–	non-eutectic	–
1.2	eutectic	–	transitional	8.0838e-1
1.3	eutectic	–	transitional	7.2477e-1

Table 16 – Categorization of solidification process into eutectic, non-eutectic, or changing from latter to former at the time τ_{eut} , and the position $Y_{\text{eut}} = Y_s(\tau_{\text{eut}})$.

R	Eutectic region	
	Scheil	lever rule
1.0	100.0	0.0
1.1	100.0	0.0
1.2	100.0	2.74
1.3	100.0	5.08

Table 17 – Percentage (%) of final domain that solidified under eutectic conditions.

5.5.4 Validation

The validation of numerical results presented in this Chapter is performed by a comparison against numerical data available in the literature. Moreover, the conservation of solute is invoked in order to attest the validity of obtained results. A mesh independence and tolerance study are also conducted to make sure the numerical results are not affected by mesh resolution or numerical errors.

5.5.4.1 Similarity Solution

To validate the similarity solution, the obtained results are compared against those given in Figs. 3 and 4 in (VOLLER, 1997); the comparisons are given in Fig. 5.34. Fig. 5.34(a) shows the results when using the Scheil assumption, whilst Fig. 5.34(b) shows the results when using the lever rule. In both cases, the superheat is taken to be just 1K.

These results, as pointed out in (VOLLER, 1997), show a concentration referred to as the intrinsic volume average that can be calculated by a given solid fraction and temperature profile, and solving the differential equation

$$\frac{d\chi < C >}{d\eta} = T \frac{k_p}{m} \frac{d\phi}{d\xi} - \beta \phi \frac{k}{m} \frac{dT}{d\xi}, \quad (5.152)$$

where χ is used as the liquid fraction, k and m , are the partition coefficient and the slope of liquidus line, respectively, and η is the similarity variable.

Figure 5.34 – Comparison for the mixture concentration with the results in (VOLLER, 1997) for: (a) $\beta = 0$; (b) $\beta = 1$. Adapted from (ASSUNÇÃO; VYNNYCKY; MITCHELL, 2020).

Also, note that these results have been computed using $T_m = 921$ K, which is the value given in (SWAMINATHAN; VOLLER, 1997; VOLLER, 1997; VOLLER, 1998; VOLLER; MOUCHMOV; CROSS, 2004), but is neither the value given in Table 8, nor the correct value for the Al-Cu phase diagram which forms the basis of the studies. In fact, using this value for T_m and $T_{eut} = 821$ K, as quoted correctly in (VOLLER, 1997), leads to $C_{eut} = (T_m - T_{eut})/m \approx 29.5$ wt%, which is lower than the value given in Fig. 5.2. In order to carry out the comparison, the definitions for the similarity variable and mixture concentration were used as given by equations (11) and (28), respectively, in (VOLLER, 1997). All of these comments notwithstanding, we can see that very good agreement has been obtained in both sub-plots of Fig. 5.34.

There is, nevertheless, a fundamental difference in the interpretation of this result: in (VOLLER, 1997), it is intended as being the profile for C for all time as a region of semi-infinite melt solidifies, whereas in our context, it is the small-time solution for an initially finite region of melt. This may help to explain an unusual feature of the result in (VOLLER, 1997): namely, that the fully solidified region has uniform composition.

Translating back from the similarity variable to physical space variable, this would mean that the solid region has uniform composition; admittedly, this composition is higher than the initial value, as one would expect with inverse segregation, but the profile is still uniform. On the other hand, in the present analysis and computations for the small-time problem, an elevated concentration is found in the first solid to form at $x = 0$, and further computation for $t > 0$ should show that concentration falls thereafter.

5.5.4.2 Non-similar Solution

The final solute concentration profiles addressed in Figs. 5.26–5.27 may have their validity attest by checking the conservation of solute across the solidified domain. This calculation was carried out in the form of eq. (5.153), with the upper bound of the integral varying from the

Figure 5.35 – Summation of final solute concentration for:(a) $\beta = 0$; (b) $\beta = 1$.

initial solid interface position to the domain final length,

$$C_{\text{total}} = \int_{Y_s^0}^{Y_m^{\text{final}}} \rho C_{\text{solid}} dY. \quad (5.153)$$

The results are presented in Fig. 5.35.a where the total solute concentration across the solidified domain adds up to the initial concentration c_0 , as it was expected. The corresponding computations were also executed considering the lever rule and the resulting concentration profile shown in Fig. 5.27 and evaluated in Fig. 5.35.b.

Fig. 5.36 shows a study on mesh independence for the spatial discretization where the solute concentration profile is shown for meshes with different number of elements, considering Scheil assumption and $R=1.3$, where N denotes the number of elements inside the mush region. Using the initial geometry data in Table 10, the size of the elements $h = (Y_l - Y_s)/N$ is varying from $h \sim 1.83 \times 10^{-4}$ to $h \sim 1.14 \times 10^{-5}$. The profiles approximately on top of each other confirms that the result does not vary among considerably fine meshes, as desirable. Each computation takes under 300 seconds on a laptop with an Intel Core i7-9750HQ CPU 2.60GHz processor and 16GB RAM.

A study on the solver tolerances is presented in Fig. 5.37, which shows the solute concentration profile with absolute and relative tolerances are equally defined ($R = A_k = \text{tol}$) varying by three orders of magnitude, considering Scheil assumption and density ratio $R = 1.3$. Once again, the profiles approximately on top of each other confirms that the result does not vary for tolerances below 1×10^{-2} .

Figure 5.36 – Final solute concentration across solidified domain for different mesh sizes. Considering $\beta = 0$ and $R = 1.3$.

Figure 5.37 – Final solute concentration across solidified domain for tolerances. Considering $\beta = 0$ and $R = 1.3$.

CONCLUSIONS AND FUTURE WORKS

6.1 Summary

In the two-dimensional macrosegregation model it can be noticed that the regions with constant values of liquid fraction are distributed across the domain, in agreement with the expected results, while the macrosegregated regions were found in the simulation as in the original paper (AMBERG, 1991) greater than average solute concentration in the upper region, and lower than average at the bottom. Besides that, the flow re-circulation in the liquid region is in an opposite direction to that in the mushy region, also compared favorably with the existing theory (FREDRIKSSON; ÅKERLIND, 2012). However there is the need for an artificial numerical parameter also required by (AMBERG, 1991; ASSUNÇÃO; VYNNYCKY, 2018) that is normally used to achieve numerical convergence. Such mechanism is not necessary for the one-dimensional, multi-domain model, this is because the governing equations are far from the usual advection-diffusion form that is suitable for computational fluid dynamics, but consist of a diffusionless transport equation, (5.23), and an algebraic relation, (5.29).

A detailed investigation around state of the art multi-domain formulations lead to the discover of flaws in the existing models, posed on the one-dimensional, semi-infinite domain, regarding the boundary conditions that defined the nature of the eutectic/non-eutectic reactions and the initial conditions as in the use of small superheat. The simplifications in the models were also prohibitive when trying to apply the existing formulations to a finite domain. Such scenario encouraged the development of the novel formulation discussed in this thesis.

The wider significance of the results for the similar one-dimensional problem is that they may provide the correct initial conditions for solving the full non-similar problem, i.e. for the solidification of the entire melt. In particular, they appear to give a framework for solving the problem using a moving mesh formulation, rather than the more commonly-used enthalpy formulation, which employs a fixed mesh. In addition, this approach would be well-suited not

just to problems involving two moving boundaries, but also when the boundaries are not planar, as was demonstrated in (VYNNYCKY; KIMURA, 2007; VYNNYCKY; KIMURA, 2015) for the two-dimensional problem of the solidification of one-component material in the presence of natural convection in an enclosure. By tracking the solid and liquid interfaces explicitly, it is hoped to be able to avoid the usual issues of numerical dispersion and diffusion that are present in the numerically simulated macrosegregation profiles reported in the literature (DU; ESKIN; KATGERMAN, 2009; VUŠANOVIĆ; VOLLER, 2014; VUŠANOVIĆ; VOLLER, 2016).

Solving the full-time non-similar problem, it was observed that whilst a composition gradient is indeed required for macrosegregation, this must be created by a relative motion between the solid and melt in the mush, i.e. a relative velocity. If $R = 1$, there is no relative velocity and hence no macrosegregation. This is more easily observed by setting $\chi = 0$ and use the lever rule ($\beta = 1$). At the solid front, the obtained solute concentration equals the initial value c_0 ; this value will remain unchanged at that position in the solid and make up the final solidified material. Once the solidification is complete, we will have $C_s \equiv C_0$ for all y , and hence no macrosegregation. Note incidentally that even when $R = 1$, there will be a compositional gradient across the mush, since there is a definitely thermal gradient, yet there will be no macrosegregation in the final solidified material. When $R > 1$, it was verified the occurrence of heterogeneous solute concentration whose severity increases with the density ratio and, therefore, with thermal gradient.

6.2 Originality

The one-dimensional model considering the solidification of a binary alloy undergoing shrinkage was formulated for the first time in the literature for a finite domain, with arbitrarily large superheat able to account for eutectic or non-eutectic solidification.

This can be seen as the simplest possible configuration for the occurrence of macrosegregation, and therefore constitutes an invaluable benchmark for the testing of numerical codes that model these phenomena.

It is important to say that the developments presented here for the multi-domain approach, when compared to earlier works on one-phase Stefan problem as (MITCHELL; VYNNYCKY, 2014), is considerable more complex by a number of factors, e.g., existence of three domains (solid, mush, liquid); three moving boundaries; a multiplicity of governing equation, that are not all parabolic partial differential equations, but also hyperbolic or algebraic; the existence of interface conditions, instead of boundary conditions only, that are not given explicitly but must be iterated for and does not follow a fixed expression, as it is liable to change due to its dependency on the values of c_0 , β and R .

As a result, an earlier-obtained solution for this problem was extended (VOLLER, 1997), that was posed on a semi-infinite spatial domain and valid for the case of low superheat and

eutectic solidification, to the more general situation. In so doing, it was found that a similarity solution is available only for short times and that this contains a boundary layer on the liquid side of the mush-liquid interface. Note that this boundary layer seems somewhat unexpected, since the usual reason for the appearance of a boundary layer - namely, a small dimensionless parameter multiplying the highest order derivative in a differential equation, as occurs in (MCCUE; WU; HILL, 2008) for large Stefan number - does not occur; instead, it seems only to have become prominent because of a series of transformations that were essential for considering the small-time behaviour of the problem.

Moreover, it is believed that this small-time solution constitutes the correct initial condition for the subsequent numerical solution of the full non-similar problem. The procedure that was adopted here, i.e. formulating a system of PDEs which becomes degenerate as $t \rightarrow 0$ when there is no solid or mush, thereby requiring a self-starting similarity solution, is analogous to that which have been used with success in a number of similar, albeit slightly simpler, solidification problems that have involved both a pure material, having a distinct phase-change temperature (MITCHELL; VYNNYCKY, 2009; MITCHELL; VYNNYCKY, 2014; MITCHELL; VYNNYCKY, 2016), and alloys having solidus and liquidus temperatures (VYNNYCKY; SALEEM, 2017; VYNNYCKY; SALEEM; FREDRIKSSON, 2018). Admittedly, however, none of these problems involved a square-root singularity in the velocity, but the fact that a self-consistent reduction of the full PDEs to ODEs was presented in the limit as $t \rightarrow 0$, in a manner analogous to that in (MITCHELL; VYNNYCKY, 2009; MITCHELL; VYNNYCKY, 2014; MITCHELL; VYNNYCKY, 2016; VYNNYCKY; SALEEM, 2017; VYNNYCKY; SALEEM; FREDRIKSSON, 2018), is a positive sign.

6.3 Significance

Macrosegregation and shrinkage cavity are two problems of great industry interest that challenge the scientific research work to this day. The development of advanced models with higher accuracy usually leads to restrictive computational costs, while the analysis through similarity transformation offers low-cost reliable solutions while providing important insights into the solution structure.

Although there still is room for improvement, the 2D solidification shrinkage model is able to verify the efficiency of the *hot-top* as an apparatus to reduce the height of the shrinkage cavity in steel ingots. While the macrosegregation models could test configurations that lead to different degrees of macrosegregation, reducing costs when designing a new alloy and providing ability to make more educated guesses instead of resorting to the trial and error approach.

In fact, according to (FREDRIKSSON; ÅKERLIND, 2006), attempts are made to keep the casting temperature as low as possible to make the melt solidify in the shortest possible time. While that seems like a straightforward solution to reduce the costs invested in the pro-

cess, it was observed that accelerating the solidification process alone does not guarantee the most uniform concentration profile and that the superheat also is an important aspect, in fact, better macrosegregation ratios were obtained for processes 2 to 10 % longer than the quickest configuration.

6.4 Unification

The flow of this project is directed towards the development of a two-dimensional macrosegregation model that accounts for solidification shrinkage. In this thesis, there are three steps towards that goal: a two-dimensional model for solidification shrinkage; a two-dimensional macrosegregation model without solidification shrinkage; and a one-dimensional macrosegregation model with solidification shrinkage.

All the aspects from each part of this work may come together to create a more complex model to tackle on a rather difficult problem and present a formulation that is still nonexistent in the literature. In that sense, the efforts to treat the one-dimensional non-similar problem in its moving boundary form, prior to the Landau transformations, corroborates to the task of expanding the current multi-domain model to a 2D formulation with solidification shrinkage and macrosegregation, at the same time as the similarity solution can also provide a starting point to a consistent initialization of single-domain models.

6.5 Future work

This work is settled to advance with the expansion of the multi-domain model to the two-dimensional domain, following (VYNNYCKY; KIMURA, 2007), where the shrinkage cavity will be an indispensable factor in defining the ingot final geometry.

The multi-domain approach can be expected to present some difficulties on modelling the formation of A-segregations as the domain shapes become too extreme. Under the same circumstances, the single-domain approach would rely on highly refined mesh to provide accurate results. Nevertheless, the multi-domain formulation is expected to provide a fruitful analysis on determining the criterion for the onset of A-segregations. The occurrence of this phenomenon is studied in (RAD; KOTAS; BECKERMANN, 2013), where the criterion is calibrated using available experimental data for ingots involving several different steel compositions and could provide a remarkable validation for this formulation.

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NON-SIMILAR – TWO REGIONS MODEL REPORT

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PUBLICATIONS

This research has contributed so far with two publications, the first in the field of single-domain modelling to the Brazilian Society of Mechanical Engineering and Sciences, ABCM - RETERM. And the second in the field of multi-domain modelling to the European Journal of Applied Mathematics.

1) ASSUNÇÃO, M.; VYNNYCKY, M.; MITCHELL, S. L. On small-time similarity-solution behaviour in the solidification shrinkage of binary alloys. **European Journal of Applied Mathematics**. Published by Cambridge University Press, (2020). DOI:10.1017/S0956792520000091

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Other publications include the research on mathematical modelling of vanadium redox batteries, partially developed during internship at the University of Limerick, Ireland, financed by São Paulo Research Foundation, grant # 2019/09418-4

3) VYNNYCKY, M.; ASSUNÇÃO, M. On the significance of sulphuric-acid dissociation in the modelling of vanadium redox flow batteries. **J Eng Math** 123, 173–203. (2020). DOI: 10.1007/s10665-020-10061-8

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