

Modelling Scheil Cooling of a Metal Alloy – Thermodynamic and Multiphysics Solidification

Tanai Marin-Alvarado*¹

¹M4Dynamics

*1 Yonge St. Suite 1801, Toronto, ON, M5E1W7, tanai.marin@m4dynamics.com

Abstract: During solidification of a multicomponent liquid, either a metal alloy, a sulphide matte or an oxide slag system, the process is highly dependant not only on temperature but also on the composition of the system.

The thermodynamic properties of the system will dictate what phases or mixtures precipitate from the liquid and their compositions. In a real solidification case, in which the system doesn't have time to constantly reach chemical equilibrium, it can be considered that once a fraction of the system has solidified it can be "removed" from the system, leaving a liquid that is now enriched of one of the components and different from the original liquid composition. As the temperature continues to decrease, a portion of this "new" liquid will solidify, generating a solid that is different in composition to the previous solids. This process continues until the last portion of liquid, now very enriched, solidifies into a solid that has a composition far from the original liquid. This is known as Scheil cooling or real solidification process and its has direct applications and importance to industrial metallurgical systems^[1,2]. A 0D analysis of this process results in the well known Scheil equation for real solidification, which has been implemented in COMSOL in this work. In addition, based on the derivation of Scheil equations, a time dependant source term to express the rate of "enrichment" of one of the components in the liquid phase has been derived and it is used to model its concentration as a function of the solid fraction function. In a 0D model, the latter is calculated using the thermodynamic library M4Dlib^[3] and it is implemented in COMSOL Multiphysics using a global ODE in order to access its time derivative. Therefore a fixed solid fraction function cannot be used to model the real solidification process. In this paper, a combined Thermodynamic and Multiphysics model was used to simulate this process using COMSOL Multiphysics® and M4Dlib®^[3].

Keywords: Solidification, Scheil cooling, Thermodynamic equilibrium, Multicomponent phase change, M4Dlib.

1. Scheil Solidification - 0D case

1.1 Thermodynamic System

Consider a binary liquid alloy with components A and B . Initially the system is at a temperature T_0 [K] such that it is fully liquid ($T_0 > T_{liquidus}$) and the initial composition of the liquid is given by X_{B0} , where X_{B0} is the mole fraction of B and $X_{A0} = 1 - X_{B0}$ is the composition of A . The excess Gibbs free energy of mixing for the liquid and solid solutions are described by the following equation:

$$G^{ex} = X_A \cdot X_B \cdot L_{AB}^{(0)} \quad \text{eq. 1}$$

with the following parameters for the solid and liquid alloys, respectively:

$$L_{AB,S}^{(0)} = 0 + 14.9094 \cdot T \quad \text{eq. 2}$$

$$L_{AB,L}^{(0)} = 0 + 7.45469 \cdot T \quad \text{eq. 3}$$

The Gibbs free energy (in J/mol) for the pure compounds A and B for solid and liquid states is given the following expressions, respectively:

$$G_{A,S}^o = -26354.125 - 22.5 \cdot T \quad \text{eq. 4}$$

$$G_{A,L}^o = 2292 - 45 \cdot T \quad \text{eq. 5}$$

$$G_{B,S}^o = -17902.75 - 15 \cdot T \quad \text{eq. 6}$$

$$G_{B,L}^o = -1805.5 - 30 \cdot T \quad \text{eq. 7}$$

Figure 1 shows the resulting phase diagram calculated using the external function library M4Dlib in COMSOL Multiphysics using the Gibbs energy minimization routines previously described^[3].

1.2 Source term: rate of "enrichment"

In this 0D model, X_{BL} is defined as the composition of component B in the liquid phase as a function of time. The time accumulation term is defined by a source representing the rate of generation or consumption of B as follows:

$$\frac{\partial X_{BL}}{\partial t} = R_{BL} \quad \text{eq. 8}$$

where X_{BL} is the mole fraction of B in the liquid phase, R_{BL} [1/s] is the rate of enrichment or depletion of component B in liquid due to the solidification process and t is the time in [s]. It is necessary to calculate R_{BL} as a function of the solidification process, taking into account that the solid that has formed in previous iterations does not equilibrate with the remaining liquid.

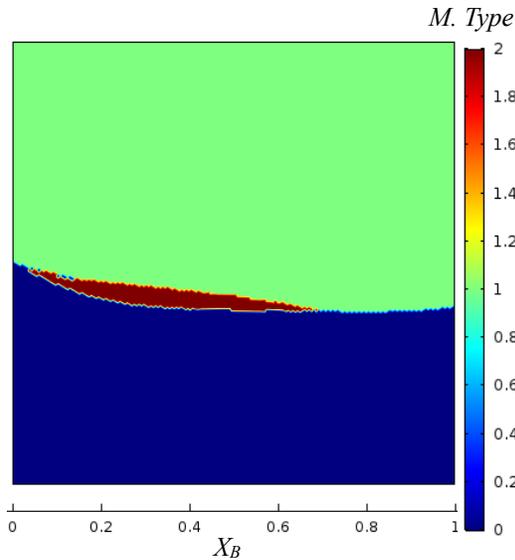


Figure 1. Calculated phase diagram for system A-B. Surface plot represents mixture type: 0 = solid alloy, 1 = liquid alloy; 2 = Solid + Liquid. Temperature from 273 to 2273 K (y axis).

R_{BL} can be derived in a similar manner to the derivation of Scheil equations. Consider the composition of component B as a function of the solid fraction at a given time $t=t_2$ as shown in Figure 2.

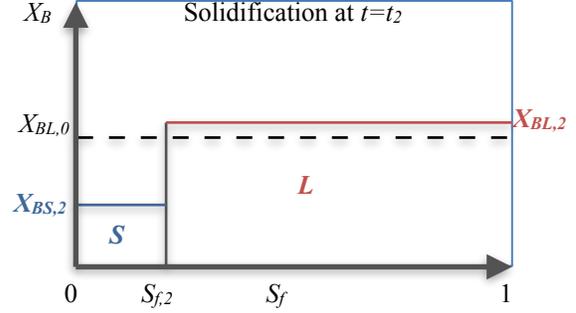


Figure 2. X_B vs Solid Fraction S_f at $t=t_2$.

The balance between the amount of B rejected into the liquid and the increase in the number of atoms of B into the liquid from time t_2 to t_3 is given in Equation 9.

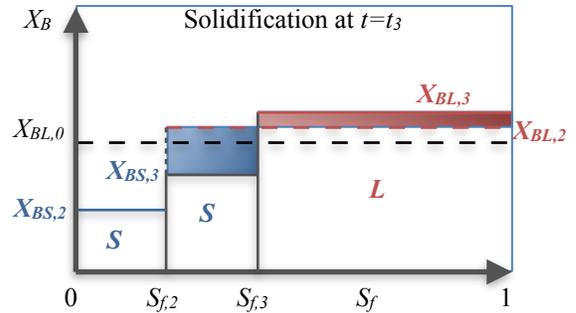


Figure 3. X_B vs Solid Fraction S_f from $t=t_2$ to $t=t_3$.

$$(S_{f,3}-S_{f,2}) \cdot (X_{BL,2}-X_{BS,3}) = (X_{BL,3}-X_{BL,2}) \cdot (1-S_{f,3}) \quad \text{eq. 9}$$

The left hand side on the above balance corresponds to the area shaded in blue in Figure 3, whereas the right hand side is the red area in Figure 3. Equation 9 can also be expressed in the following differential form:

$$(X_{BL}-X_{BS}) \cdot \partial S_f = (1-S_f) \cdot \partial X_{BL} \quad \text{eq. 10}$$

Considering that the change in composition and solid fraction took place from time t_2 to t_3 , then the time differential for this quantities is:

$$(X_{BL}-X_{BS}) \cdot \frac{\partial S_f}{\partial t} = (1-S_f) \cdot \frac{\partial X_{BL}}{\partial t} \quad \text{eq. 11}$$

Rearranging Equation 11, the rate of enrichment or depletion of component B in equation 8 corresponds to the right hand side of Eq. 12 below:

$$\frac{\partial X_{BL}}{\partial t} = \frac{(X_{BL}-X_{BS})}{L_f} \cdot \frac{\partial S_f}{\partial t} \quad \text{eq. 12}$$

To calculate the rate of change of X_{BL} , it is necessary to calculate the time derivative of the solid fraction function, the liquid fraction and the current composition of B in liquid and solid phases during solidification. This will be described later in the implantation section.

1.3 Scheil equations

The partition coefficient is defined as the ratio between the solid and the liquid concentration of component B , as follows:

$$K_{BS,L} = \frac{X_{BS}}{X_{BL}} \quad \text{eq.13}$$

therefore, equation 10 can be rewritten as:

$$(X_{BL} - K_{BS,L} \cdot X_{BL}) \cdot \partial S_f = (1 - S_f) \cdot \partial X_{BL} \quad \text{eq.14}$$

rearranging and integrating from the initial state at $S_f = 0$ and $X_B = X_{B0}$ to a given point during the solidification process (S_f, X_{BL}), the following is obtained:

$$(1 - K_{BS,L}) \int_0^{S_f} \frac{\partial S_f}{(1 - S_f)} = \int_{X_{B0}}^{X_{BL}} \frac{\partial X_{BL}}{X_{BL}} \quad \text{eq.15}$$

Note that in Equation 15 it is assumed that the partition coefficient between solid and liquid concentration is constant, which is not necessarily true for all thermodynamic systems. Solving and evaluating the integrals in Equation 15 above yields:

$$(K_{BS,L} - 1) \cdot \ln(1 - S_f) = \ln \frac{X_{BL}}{X_{B0}} \quad \text{eq.16}$$

From which the expressions to calculate the concentration of B in both the liquid and solid phases are obtained:

$$X_{BL} = X_{B0} \cdot (1 - S_f)^{(K_{BS,L} - 1)} \quad \text{eq.17}$$

$$X_{BS} = K_{BS,L} \cdot X_{B0} \cdot (1 - S_f)^{(K_{BS,L} - 1)} \quad \text{eq.18}$$

2. Implementation of 0D Scheil Cooling in COMSOL Multiphysics®

To demonstrate the concept of real solidification using Scheil cooling approximation a 0D model was used. Start by selecting 0D as space dimension and “Global ODEs and DAEs” from the Mathematics branch in the Physics selection, followed by time dependent study.

A set of parameters have been defined under Global Definitions. These are summarized in Table 1.

To calculate the solid fraction and equilibrium concentrations, the external function library M4Dlib is used by selecting “Functions”, then “External”, from the Global Definitions node. The functions used from M4Dlib are listed in Table 2.

Table 1: Global Parameters

Name	Expression	Descr.
R	-1[K/s]	Temperature decrease rate
XA0	0.5	initial concentration of A
XB0	1-XA0	initial concentration of B
T0	1155[K]	Initial Temperature

Table 2: Functions defined in M4Dlib external library

Function name	Arguments
Sf_slow	T, XA, XB
XAs_slow	T, XA, XB
XAl_slow	T, XA, XB

The functions above defined in M4Dlib correspond to the equilibrium solid fraction and composition of component A in solid and liquid as a function of the local temperature T and system compositions (X_A and X_B).

The file containing the thermodynamic information for the pure compounds A and B and the solid and liquid solution models is “M4Dlib_system_DB_iso.txt” and is specified in the “initialization data” on the “Advanced” tab under the settings of the External function.

Three dependent variables: T , S and XB , are declared in the Global ODEs and DAEs (ge) node under Global Equations as described in Table 3.

T represents the temperature of the system which is controlled by a simple rate term to simulate a constant decrease in temperature. The expression for T in Table 3 is equivalent to:

$$\frac{\partial T}{\partial t} = R \quad \text{eq.19}$$

where R was defined in Table 1 as a global parameter.

Table 3: Global Parameters

Name	f(u,ut,utt,t)	Initial value
T	Tt-R	T0
S	S-Sf_slow(T,XA0,XB0)	0
XB	XBt-RBL	XB0

The second dependent variable, S , represents the solid fraction function and it is defined as:

$$S = S_{f,slow}(T, X_{A0}, X_{B0}) \quad \text{eq.20}$$

where Sf_slow is calculated by the external function library M4Dlib using Gibbs energy minimization.

Finally, the change in liquid composition taking into account the enrichment (or depletion) of component B due to rapid solidification is given by the third equation in Table 4, which corresponds to Equation 8.

The term RBL in Table 3 is defined within the “variables” definitions for Component 1 along with the rest of the required variables shown in Table 4.

3. Results

3.1 Scheil Cooling

As the temperature decreases due to the imposed rate of temperature decrease, R , the liquid reaches the liquidus temperature for the given system composition X_{B0} at 1125.7 K. At this point, the first solid to appear has a composition of 0.171 (mole fraction) of component B and the liquid of 0.518. Figure 4 shows the calculated liquid and solid phases composition based on Equation 8 and 18, respectively as a function of Absolute Temperature.

As expected, the concentration of both solid and liquid phases increases as the temperature decreases. In Figure 4, the composition of B in the solid phase represents the composition of the last solid to solidify at a given temperature rather

than the average composition of the solid. It can be seen in Figure 4 how the solid that precipitates, reaches concentrations that go beyond the initial system concentration X_{B0} , which could not be the case if full thermodynamic equilibrium is reached at all times. This is the effect of Scheil cooling or rapid solidification.

Table 4: Variables for Component 1

Name	Expression	Descr.
Sf	comp1.S	solid fraction
Lf	1-comp1.S	liquid fraction
XAs_eq	XAs_slow(comp1.T, XA0, XB0)	equilibrium concentration of A in solid
XAl_eq	XAl_slow(comp1.T, XA0, XB0)	equilibrium concentration of A in liquid
XBs_eq	(Sf>0)*(1-XAs_eq)	equilibrium concentration of B in solid
XBl_eq	(Lf>0)*(1-XAl_eq)	equilibrium concentration of A in liquid
KBsl	(XBl_eq>0)*(XBs_eq/XBl_eq)	partition coefficient
XBs_Scheil	KBsl*XB0*(1-Sf)^(KBsl-1)	Last solid concentration, Scheil cooling
XBl_Scheil	XB0*(1-Sf)^(KBsl-1)	Concentration of liquid, Scheil cooling
RBL	comp1.St*(XBl_3-XBs_3)/(Lf+eps)	Source term for equation 8

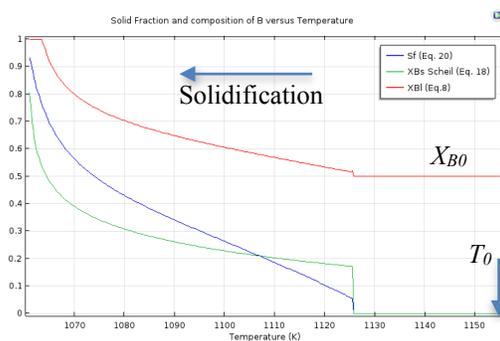


Figure 4. Solid and liquid composition of component B and Solid Fraction versus Absolute Temperature.

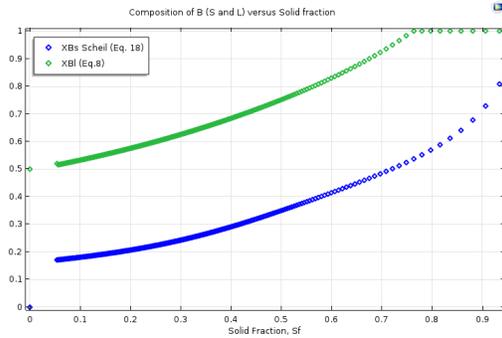


Figure 5. Solid and liquid composition of component *B* versus Solid Fraction.

The concept of rapid solidification or Scheil cooling previously shown in Figures 2 and 3 is now shown in Figure 5 for the calculated results.

Note that the composition of *B* in the liquid phase in Figures 4 and 5 was limited to 1. This is probably due to the assumption of a constant partition coefficient throughout the entire composition range, which clearly isn't true for this thermodynamic system.

3.2 Equilibrium Cooling

As a mode of comparison, the calculated equilibrium composition for solid and liquid phases given by *XBs_eq* and *XBl_eq*, respectively (defined in Table 4), as well as the Solid fraction function are shown in Figure 6. In this case, the final solid composition is the same as the starting composition of the liquid, which is expected if the system reached equilibrium at all times.

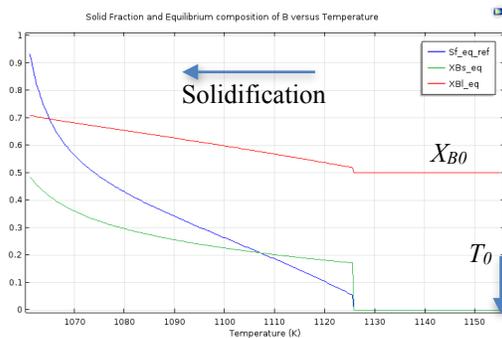


Figure 6. Solid and liquid equilibrium composition of component *B* and Solid Fraction versus Absolute Temperature.

3.3 Modified Scheil or Real Cooling

One of the limitations of Scheil cooling equations is the assumption of a constant partition coefficient, $K_{BS,L}$. Equations 17, 18 and

the source term R_{BL} defined in Table 4 for equation 8 are based on this assumption. This is a good approximation in cases where the system shows eutectic solidification and the Scheil equations are valid until the eutectic temperature, but in the case of isomorphous systems, such as in this example, this assumption is probably good only during the initial stage of solidification. If the partition coefficient is not assumed constant and in fact considered as a function of both solid and liquid compositions, then Equation 15 is not valid and instead, the following equation has to be solved:

$$\int_0^{S_f} \frac{\partial S_f}{(1-S_f)} = \int_{X_{B0}}^{X_{BL}} \frac{\partial X_{BL}}{X_{BL}(1-K_{BS,L})} \quad \text{eq. 21}$$

The left hand side of Equation 21 can be solved in the same way as previously shown, however the right hand side will depend on the actual system since $K_{BS,L}$ depends on X_{BL} . This results in:

$$-\ln(1-S_f) = \int_{X_{B0}}^{X_{BL}} \frac{\partial X_{BL}}{X_{BL}(1-K_{BS,L})} \quad \text{eq. 23}$$

The above equation can be integrated numerically and has been implemented in M4Dlib. However, it is still not available as a function for the COMSOL external function interface. The result of equation 23 for the liquid and solid composition of *B* as a function of cumulative solid fraction is compared to the COMSOL implementation of Scheil cooling approximation in Figure 7 below.

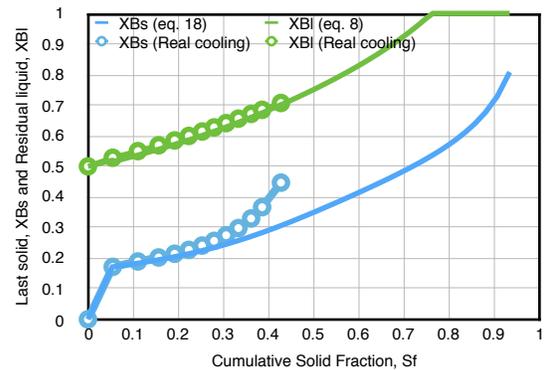


Figure 7. Solid and liquid composition of component *B* versus Solid Fraction. Comparison between Scheil cooling approximation and Real Solidification.

It is seen in Figure 7 that initially both solid and liquid compositions for the two approaches are in good agreement but the solid composition

in the case of Eq. 23 increases more rapidly than in the case of the Scheil approximation. Also, the last composition before full solidification is approximately 0.5 and 0.7 for solid and liquid phases, respectively. This is because of the shape of the phase diagram at that composition, which is not taken into account by the Scheil assumption of a constant partition coefficient.

Another important difference in the two approaches is the final temperature of the system before full solidification. In the case of the Scheil approximation implemented in COMSOL, full solidification takes place at 1060.64 K which is the same temperature as for equilibrium cooling. When the residual liquid becomes richer in component B since the solid does not equilibrate with the liquid after precipitating, it is equivalent to displacing the liquid composition further to the right than the equilibrium in the phase diagram, resulting in a lower temperature for the final liquid. This is the result when using equation 23 with a numerical integration method in M4Dlib, in which case the last liquid disappears at 1055.25 K.

4. Conclusions

An implementation of Scheil cooling using COMSOL Multiphysics® and M4Dlib® has been done using a 0D ODE model. The model defines three variables: T , S and XB for temperature, solid fraction and composition of B in the residual liquid, respectively. A source term, RBL , that depends on thermodynamics and Scheil equations is defined as a variable and used to calculate XB . These depend on the time derivative of solid fraction S , which is in turn calculated by Gibbs energy minimization routines provided by M4Dlib for a given binary system.

The results show the expected behaviour for Scheil cooling approximation, in which the last solid to precipitate has a concentration much higher than the initial composition of the system. However, the model still has some limitations. For example, the Scheil equations, and in particular the source term for XB , diverge when the liquid fraction becomes zero and the assumption of a constant partition coefficient is not valid throughout the entire composition range. In addition, the time derivative for the ODE dependent variable S is not explicitly provided in the external function and this causes numerical instability, requiring manual settings of time dependent solver. It is planned to include the time derivative of S (dS/dt) in M4Dlib by

using the temperature time derivative as an argument.

Although a 0D model was chosen to demonstrate the concept of Scheil cooling by coupling Multiphysics and Equilibrium Thermodynamics, an extension to space dependent models (1, 2 or 3D) is easily achievable with COMSOL Multiphysics.

5. References

1. P. Schaffnita, C. Stallybrassa, J. Konrada, F. Steinb, M. Weinberg, "A Scheil–Gulliver model dedicated to the solidification of steel", *CALPHAD*, vol 48, 2015, pp184-188.
2. D. Durinck, P. Tom Jones, B. Blanpain, P. Wollants, G. Mertens, J. Elsen, "Slag Solidification Modeling Using the Scheil–Gulliver Assumptions", *Journal of the American Ceramic Society*, vol 90 (4), 2007, pp. 1177–1185.
3. T. Marin-Alvarado, "Combining Multiphysics Modeling and Solution Thermodynamics Using M4Dlib, an External Library", COMSOL Conference, Boston 2015.