The Evolution of the Fraction of Individual Phases During a Simultaneous Multiphase Transformation from Time–Temperature Data

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A formal mathematical approach to cooling curve analysis of multiple simultaneous transformations is introduced for the first time. The goal of this methodology is to measure individual phase fractions during free cooling. Transformation start and end temperatures can also be accurately measured using this approach. As an example, the simultaneous solidification–precipitation in aluminum A356 alloys with varying magnesium and silicon content has been used to show the feasibility of this new method to complex transformations. The results are in good agreement with modeling results using the Scheil model of solidification.

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I. INTRODUCTION

COOLING curve analysis has been preached for long and has reached a high degree of progress.^[1-5] None of the existing literature, however, has addressed the proper treatment of multiple simultaneous phase transformations. This paper generalizes the well-established formalism of^[2] to address multiple phase transformations rigorously. Similar to previous CCA techniques, the proposed method in this paper relies on measuring the temperature of a sample as it undergoes phase transformations during Newtonian cooling. In this method the heat balance between the cooling sample and the surrounding environment is used in addition to tabulated latent and specific heat of present phases to determine the fraction of all existing phases in the sample. The main benefit of this method is that it can be used for multiple simultaneous phase transformations with the number limited by the quality of input data used, not by the mathematical formulation as in past implementations of CCA.^[1–3,6] This approach can work under a variety of cooling conditions,^[2] it requires little to none specialized machinery, facilities, computing power, and it is timesaving. These benefits are more evident when considering that these types of measurements are currently made using techniques that are either slow, expensive, or difficult to access, and in some cases, unable to accommodate realistic sample sizes or cooling rates; among those one can mention micro-scopy,^[7] differential scanning calorimetry (DSC),^[7–10] differential thermal analysis (DTA),^[11,12] synchrotron diffraction,^[13] dilatometry^[14,15] or indirect measurements such as density,^[16] magnetic field,^[17] and electrical

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resistivity.^[18] The limitations of these techniques are discussed in Reference 3.

Current CCA techniques are limited to tracking formation temperatures and phase fractions for *separate* phase transformations (*e.g.*, solidification OR precipitation). The method presented here does not suffer from such a limitations and can be used for complex phase transformations such as precipitation during solidification in aluminum alloys or potentially for the austenite to pearlite/martensite/ferrite transformation in steels. A more complex example of the application of the proposed methodology is in the welding of pipeline microalloyed steels (*e.g.*, X70, X80, and X100). These steels tend to form more than 5 phases upon cooling from austenite.^[19] These phases can be any combination of ferrite, bainite, pearlite, martensite, TiN, Nb(C,N), V(C,N), and complex precipitates.

The general mathematical approach presented in the next section is compared against the simultaneous solidification and precipitation of ten variants of aluminum alloy A356.

II. THERMODYNAMIC BALANCE DURING MULTIPLE TRANSFORMATIONS

An important aspect of the proposed methodology is to assign a single temperature to the whole sample (Newtonian cooling). To achieve this goal, any experiment conducted must have a small Biot number (Bi = $\bar{h}_{eff}L_c/k < <1$, where \bar{h}_{eff} is the average effective heat transfer coefficient (accounting for convection, radiation, and insulation), L_c a characteristic length defined as $L_c = V/A_s$, where V and A_s are, respectively, the volume and surface area of the sample, and k is the thermal conductivity of the sample).^[20] In this methodology, special care is taken to ensure that the heat transfer coefficient (\bar{h}_{eff}) is constant during cooling.

Without loss of generality, consider a sequence of phase transformations $1 \rightarrow 2, 1 \rightarrow 3, \dots, 1 \rightarrow n$

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taking place at different time scales during cooling with Phase 1 being the only parent phase. An example of this transformation sequence is the precipitation of intermetallics in the interdendritic region of aluminum alloys during solidification. The precipitation in the solid during solidification requires a different sequence of transformations $(1 \rightarrow 2, 1 \rightarrow 2 \& 2 \rightarrow 3)$ that can be analyzed with slight modifications to the derivations presented here.

The heat of transformation (ΔH_{ij}) is approximately constant in the temperature range between start and end of transformation. For example, in the precipitation of Mg₂Si in aluminum alloys, the latent heat of precipitation of Mg₂Si from the liquid phase is $\Delta H = -476.5$ J/g at 829.7 K (556.5 °C) (beginning of precipitation for Alloy 6 discussed later in Table II. Alloy 6 displays the largest amount of precipitation of all alloys considered) and $\Delta H = -467.9$ J/g at 772.4 K (499.2 °C) (end of precipitation for Alloy 6).^[21] In this example, there is only a 1.8 pct change in the latent heat of precipitation from the beginning to the end of precipitation. In the analysis that follows, the heat of transformation will be considered constant.

For an experimental setup based on convective cooling, an energy balance indicates that all enthalpy released during cooling and phase transformations is balanced by the heat losses by convection at the surface of the sample. For a small amount of cooling, -dT, the enthalpic balance of the system is represented by:

$$- mf_1c_{p_1}dT - mf_2c_{p_2}dT - mf_3c_{p_3}dT - \dots - mf_nc_{p_n}dT$$
$$+ m\Delta H_{12}df_2 + m\Delta H_{13}df_3 + \dots + m\Delta H_{1n}df_n$$
$$= \bar{h}_{eff}A_s(T - T_\infty)dt$$
[1]

This equation accounts for multiple phases present at any given temperature, with those that are not present having a mass fraction (f) of zero. To adapt this formulation to a three-phase system, the value of nshould be replaced by 3 and no new terms should be added. The symbols used are described in Table I. The terms containing dT in Eq. [1] represent the amount of heat released by the corresponding phase during cooling. The terms containing df_i represent the latent heat ature-dependent variable (f_i^*) that ranges from 0, before the transformation, to 1, after the transformation is complete and a constant (f_i^c) , corresponding to the characteristic mass fraction of Phase *i*). The summation of the mass fraction of all phases equals one: *i.e.*, $\sum_{i=1}^{n} f_i = 1$ and $\sum_{i=2}^{n} f_i^c = 1$.

$$\frac{\overbrace{c_{p_{1}}}^{\alpha_{1}}}{K'} dT + \underbrace{\overbrace{c_{p_{2}} - c_{p_{1}}}^{\alpha_{2}}}_{K'} f_{2}^{*} f_{2}^{*} dT + \underbrace{\overbrace{c_{p_{3}} - c_{p_{1}}}^{\alpha_{3}}}_{K'} f_{3}^{*} dT + \cdots + \underbrace{\overbrace{c_{p_{n}} - c_{p_{1}}}^{\alpha_{n}}}_{K'} f_{n}^{*} dT - -\underbrace{\underbrace{\Delta H_{12}}_{K'} f_{2}^{c}}_{\beta_{2}} df_{2}^{*} - \underbrace{\underbrace{\Delta H_{13}}_{K'} f_{3}^{c}}_{\beta_{3}} df_{3}^{*} \qquad [2] \\ - \cdots - \underbrace{\underbrace{\Delta H_{1n}}_{K'} f_{n}^{c}}_{\beta_{n}} df_{n}^{*} = -(T - T_{\infty}) dt$$

Equation [2] can be further rearranged to group similar terms together and only leave out terms related to Phase 2 as shown below:

$$\begin{cases} \overbrace{\left(\alpha_{1}+\alpha_{3}f_{3}^{*}+\dots+\alpha_{n}f_{n}^{*}-\beta_{3}\frac{df_{3}^{*}}{dT}-\dots-\beta_{n}\frac{df_{n}^{*}}{dT}\right)}^{\gamma_{2}}dT \\ +\alpha_{2}f_{2}^{*}dT-\beta_{2}df_{2}^{*}=-(T-T_{\infty})dt \\ \gamma_{2}dT+\alpha_{2}f_{2}^{*}dT-\beta_{2}df_{2}^{*}=-(T-T_{\infty})dt \end{cases}$$
[3]

A similar procedure can be done to obtain equations similar to Eq. [3] for all other phases. In relevance to the development of the current model, the equations for Phase 3 and Phase n are shown below:

$$\begin{cases} \overbrace{\left(\alpha_{1}+\alpha_{2}f_{2}^{*}+\dots+\alpha_{n}f_{n}^{*}-\beta_{2}\frac{df_{2}^{*}}{dT}-\dots-\beta_{n}\frac{df_{n}^{*}}{dT}\right)}^{\gamma_{3}}dT \\ +\alpha_{3}f_{3}^{*}dT-\beta_{3}df_{3}^{*}=-(T-T_{\infty})dt \\ \gamma_{3}dT+\alpha_{3}f_{3}^{*}dT-\beta_{3}df_{3}^{*}=-(T-T_{\infty})dt \end{cases}$$

$$[4]$$

$$\begin{cases} \overbrace{\left(\alpha_{1} + \alpha_{2}f_{2}^{*} + \alpha_{3}f_{3}^{*} + \dots + \alpha_{n-1}f_{n-1}^{*} - \beta_{2}\frac{df_{2}^{*}}{dT} - \beta_{3}\frac{df_{3}^{*}}{dT} - \dots - \beta_{n-1}\frac{df_{n-1}^{*}}{dT}\right)}^{\gamma_{n}} dT \\ + \alpha_{n}f_{n}^{*}dT - \beta_{n}df_{n}^{*} = -(T - T_{\infty})dt \\ \gamma_{n}dT + \alpha_{n}f_{n}^{*}dT - \beta_{n}df_{n}^{*} = -(T - T_{\infty})dt \end{cases}$$
[5]

released do to the corresponding phase transformation. The term on the right hand side of Eq. [1] describes the heat transferred to the surrounding environment.

Equation [1] can be rearranged as Eq. [2] where $K' = \bar{h}_{eff}A_s/m$ and $f_i = f_i^c f_i^*$ (f_i is split up into a temper-

 α_1 represents the material before any transformation has started (*i.e.*, the portion of the cooling curve before t_{S_2} in Figure 1 where $f_2^*, f_3^*, \ldots, f_n^*$ and $df_2^*, df_3^*, \ldots, df_n^*$ are all zero). Therefore, we can evaluate α_1 by examining the portion of the cooling curve that only

Table I. List of Terms and Symbols Used

Symbol	Name	Units
A	mold area	m ²
C_{D_i}	specific heat capacity of Phase <i>i</i>	J/gK
f_i	actual mass fraction of Phase i	g/g
f_i^c	characteristic mass fraction of Phase i	g/g
f_i^*	normalized mass fraction of Phase i	g/g
\dot{F}_{SE}	fraction of solid at eutectic start	g/g
	temperature	
F_{SP}	fraction of solid at precipitation start temperature	g/g
K'	quantity defined in Eq. [2]	W/gK
т	total mass of the sample	g
п	index number	_
t	time	S
t_{Si}	<i>i</i> th phase formation start time	S
t_{Fi}	<i>i</i> th phase formation finish time	S
Т	measured temperature of the sample	Κ
T_E	eutectic formation start temperature	Κ
T_L	liquidus temperature	Κ
T_P	precipitation start temperature	Κ
T_{∞}	ambient temperature	Κ
α_i	quantity related to sensible heat defined in Eq. [2]	S
β_i	quantity related to latent heat defined in Eq. [2]	Ks
γ_i	quantity related to heat of all phases except Phase <i>i</i>	S
ΔH_{ij}	latent heat of transformation $i \rightarrow j$	J/g

consists of Phase 1 (section of cooling curve before t_{S2} in Figure 1). When the only phase present in the material is Phase 1, all the other phase fractions will be zero $(f_2^* = f_3^* = \cdots = f_n^* = df_2^* = df_3^* = \cdots = df_n^* = 0$ in Eq. [2]), hence we will have $\alpha_1 dT = -(T - T_\infty) dt$. This equation can be integrated to result in

$$-\frac{1}{\alpha_1} = \frac{d[\ln(T - T_\infty)]}{dt}.$$
 [6]



Fig. 1—Schematic representation of a typical cooling curve with n phases and n - 1 phase transformations.

constant and its weak dependence on temperature will be captured as a gentle slope in a graph of $d[ln(T - T_{\infty})]dt$ vs temperature.

The next step is to fit the inverse of α_1 to the experimental data (temperature vs. time) as a function of temperature (or time). This approach to evaluating α_1 does not require explicit evaluation of the individual parameters that make up α_1 (*i.e.*, c_{p_1} , *m*, *A*, *K*).

Using a similar approach as used in evaluating α_1 , one can evaluate each α_i and γ_i from a specific portion of the cooling curve. Equation 7 demonstrates how each portion of the schematic cooling curve in Figure 1 is used to evaluate α_i and γ_i .

$\begin{cases} \alpha_1 & \xrightarrow{\text{eval.from}} \text{ portion of cooling curve before } t_{S2} \end{cases}$	
$\alpha_2 + \gamma_2 \xrightarrow{\text{eval.from}} \text{portion of cooling curve after } t_{F2}$	
$\gamma_2 \xrightarrow{\text{eval.from}} \text{portion of cooling curve before } t_{S2}$	
$\alpha_3 + \gamma_3 \xrightarrow{\text{eval.from}} \text{portion of cooling curve after } t_{F3}$	
$\gamma_3 \xrightarrow{\text{eval.from}} \text{portion of cooling curve before } t_{S3}$	[7]
: repeat for every phase	
$\alpha_n + \gamma_n \stackrel{\text{eval.from}}{\longrightarrow}$ portion of cooling curve after t_{Fn}	
$\gamma_n \xrightarrow{\text{eval.from}} \text{portion of cooling curve before } t_{Sn}$	
$ \left(\alpha_1 + \alpha_2 + \alpha_3 + \dots + \alpha_n \stackrel{\text{eval.from}}{\longrightarrow} \text{ portion of cooling curve after } t_{F2} \right) $	

Because heat transfer coefficient and specific heat of all phases are nearly constant in the experimental conditions of this methodology, the value of α_1 is nearly

An example of how the values in Eq. [7] are fitted to sample experimental data in the solidification of aluminum A356 alloy is shown in Figure 2. For example, it can be seen how a straight line is an appropriate approximation to the dependence of $-1/\alpha_1$ with temperature. Points A and B in Figure 2 were chosen in a way that the line passing through these two points is the best approximation for the entire region where only Phase 1 exists. Similarly, the line passing through points C and D in Figure 2 is the best fit line to approximate the dependence of $-1/\gamma_3$ with temperature. A single line passing through points E and F in Figure 2 can be used to simultaneously show the dependence of $-1/(\alpha_3 + \gamma_3)$, $-1/(\alpha_2 + \gamma_2)$, and $-1/(\alpha_1 + \alpha_2 + \alpha_3)$ on the temperature.

$$\begin{cases} \beta_2 \xrightarrow{\text{eval.by}} \text{ forcing } f_2^* = 1 \text{ after } t_{F2} \\ \beta_3 \xrightarrow{\text{eval.by}} \text{ forcing } f_3^* = 1 \text{ after } t_{F3} \\ \vdots \text{ repeat for every phase} \\ \beta_n \xrightarrow{\text{eval.by}} \text{ forcing } f_n^* = 1 \text{ after } t_{Fn} \end{cases}$$
[8]

After evaluating α_1 , α_2 , α_3 , ..., α_n and β_2 , β_3 , ..., β_n , an Euler explicit integration scheme is applied to Eqs. [3], [4], and [5] (and similar equations for all other phases) to obtain the fraction of each phase as shown below:

$$\begin{cases} f_2^{*i+1} = f_2^{*i} + \frac{1}{\beta_2} \Big[\gamma_2 (T^{i+1} - T^i) + \alpha_2 f_2^{*i} (T^{i+1} - T^i) + (T^{i+1} - T_\infty) (t^{i+1} - t^i) \Big] \\ f_3^{*i+1} = f_3^{*i} + \frac{1}{\beta_3} \Big[\gamma_3 (T^{i+1} - T^i) + \alpha_3 f_3^{*i} (T^{i+1} - T^i) + (T^{i+1} - T_\infty) (t^{i+1} - t^i) \Big] \\ \vdots \quad \text{repeat for every phase} \\ f_n^{*i+1} = f_n^{*i} + \frac{1}{\beta_n} \Big[\gamma_n (T^{i+1} - T^i) + \alpha_n f_n^{*i} (T^{i+1} - T^i) + (T^{i+1} - T_\infty) (t^{i+1} - t^i) \Big] \end{cases}$$
[9]

Because the latent heat and the heat transfer properties in this methodology are nearly constant, the values of β_i in Eq. [2] will be considered to be constant and can be calculated by forcing the corresponding f_i^* to be equal to 1 for the portion of the cooling curve where the corresponding Phase *i* has finished forming (*i.e.*, after t_{F_i}). Hence, we have Finally, f_2^c , f_3^c , ..., f_n^c can each be separately calculated as follows:

$$\begin{cases} f_3^c = \frac{c_{p_1} \beta_3}{\alpha_1 \Delta H_{13}} \\ \vdots & \text{repeat for every phase} \\ f_n^c = \frac{c_{p_1} \beta_3}{\alpha_1 \Delta H_{1n}} \\ f_2^c = 1 - \sum_{i=3}^n f_i^c \end{cases}$$
[10]



Fig. 2—Fitting parameters in Eq. [7] to experimental data (aluminum A356) as linear functions of temperature. The numbered reactions correspond to those described in Eq. [11].

Table II. Chemical Composition of Different Aluminum A356 Alloys Used (Al Balance)

	Element (wt pct)								
	Si*	Fe**	Cu**	Mn**	Mg*	Zn**	Ti^\dagger		
Alloy 1	6.40	0.12	0.10	0.05	0.24	0.05	0.20		
Alloy 2	7.77	0.12	0.10	0.05	0.23	0.05	0.20		
Alloy 3	6.89	0.12	0.10	0.05	0.24	0.05	0.20		
Alloy 4	7.09	0.12	0.10	0.05	0.45	0.05	0.20		
Alloy 5	7.12	0.12	0.10	0.05	0.37	0.05	0.20		
Alloy 6	6.82	0.12	0.10	0.05	0.69	0.05	0.20		
Alloy 7	7.38	0.12	0.10	0.05	0.34	0.05	0.20		
Alloy 8	6.09	0.12	0.10	0.05	0.23	0.05	0.20		
Alloy 9	6.79	0.12	0.10	0.05	0.26	0.05	0.20		
Alloy 10	8.09	0.12	0.10	0.05	0.13	0.05	0.20		
*) (1									

*Measured.

**Average of nominal range. [†]Maximum allowed.



Fig. 3—Schematic representation of experimental setup.

The specific heat capacity of Phase 1, enthalpy of formation of Phase 3 to *n* from Phase 1 (*i.e.*, c_{p_1} , ΔH_{13} , ..., ΔH_{1n} in Eq. [2)] need to be looked up from standard thermochemical tables or calculated through Thermo-Calc software.

 $\begin{cases} \text{Reaction 1: } L \to Al \\ \text{Reaction 2: } L \to Al + Si \\ \text{Reaction 3: } L \to Al + Si + Mg_2Si + Al_8FeMg_3Si_6 \end{cases}$

their nominal content was chosen based on^[22] The molten alloys were poured into containers with thin insulating walls as schematically shown in Figure 3. The insulating walls along with small sample sizes minimized thermal gradients in the sample. The metal samples were heated to slightly more than 373.2 K (100 °C) above their respective liquidus temperature, poured into new containers and allowed to cool to at least 323.2 K (50 °C) below their solidus temperature.

A single type K thermocouple recording at 10 Hz frequency was used in all of the experiments (located in the center of the fiber cup as shown in Figure 3). After the molten metal was poured into the cups, a fiber insulation sheet was immediately placed on top to prevent heat losses due to radiation. In addition, the entire setup was placed in a box to prevent stray air currents from affecting the heat transfer rate of the metal sample in the cups. The recorded cooling rates were of the order of 0.15 to 0.3 K/s.

Aluminum A356 was specifically chosen as an example because of its wide industrial application, readily available thermophysical data and the fact that it shows simultaneous solidification–precipitation reactions as shown below^[22–24]:

(primary aluminum dendrites) $\sim 885.2 \mathrm{K}(612 ^{\circ}\mathrm{C})$	
(Al/Si eutectic) $\sim 853.2 \mathrm{K}(580 ^{\circ}\mathrm{C})$	[11]
$(\text{eutectic} + \text{precipitates}) \sim 823.2 \text{K}(550 ^{\circ}\text{C})$	

III. EXPERIMENTAL

To achieve Newtonian cooling conditions, relatively small samples (~ 200 to 300 cm³) of aluminum A356 alloys with compositions given in Table II were melted in SiC crucibles. The amounts of silicon and magnesium (marked with *) were varied intentionally and measured while for all other elements, the average or maximum of Reaction 1 corresponds to the solidification of primary aluminum and the beginning of formation of dendrites. Reaction 2 corresponds to the formation of Al/Si eutectic. Reaction 3 corresponds to two precipitation reactions that occur nearly simultaneously. One of the reactions is the precipitation of Mg₂Si from the liquid. The other reaction is the precipitation of Al₈FeMg₃Si₆

Table III.	Final	Mass	Fraction	of	Precipitate	Present	in	Aluminum	A356	Alloys
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	Pre					
	Present Methodology	Equilibrium	Scheil Equation	$f_{\rm Mg_2Si}$	ΔH_{13} (J/g)	
Alloy 1	0.0090	0.0096	0.0084	0.201	-132.545	
Alloy 2	0.0080	0.0094	0.0083	0.201	-132.572	
Alloy 3	0.0087	0.0096	0.0085	0.201	-132.454	
Alloy 4	0.0123	0.0129	0.0121	0.241	-149.578	
Alloy 5	0.0110	0.0116	0.0110	0.197	-130.851	
Alloy 6	0.0155	0.0167	0.0149	0.376	-206.992	
Alloy 7	0.0106	0.0112	0.0104	0.196	-130.199	
Alloy 8	0.0084	0.0094	0.0082	0.202	-132.843	
Alloy 9	0.0091	0.0099	0.0088	0.199	-131.655	
Alloy 10	0.0066	0.0079	0.0065	0.218	-139.744	



Fig. 4—Comparison of the final precipitate mass fraction obtained from the current methodology and Scheil model for the ten alloys used in this research.



Fig. 6—Precipitate fraction vs temperature forming in Alloy 6 during solidification.



Fig. 5—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 6.



Fig. 7—Schematic representation of the most important information obtained from a solid fraction curve.

(typically called "sludge" in industrial settings). Neither of these reactions is typically desirable at this stage, as sludge severely affects the mechanical properties of the final alloy (lower strength and much lower toughness), and the precipitation of Mg₂Si is desired to be in the solid state, as part of the precipitation hardening process. During these reactions, the specific heat capacity of molten aluminum, is 0.963 J/gK.^[25,26]

The role of ΔH_{13} deserves special attention and so, it is discussed in detail here. The difference in start temperature for both precipitation reactions is relatively small and undistinguishable in the experimental data collected. Thermo-Calc analysis indicates that precipitation of the sludge happens first, followed by Mg₂Si after the sample cooling progressed further 4 to10 K. Because of their near-simultaneous behavior, both precipitation reactions are treated as a single one with a heat of formation given by the following mass fraction average:

Table IV. Critical Information Obtained from the Phase Fraction Curves Similar to Figs. 5 and 6 for All Studied Alloys

	T_L (°C)		T_E (°C)		T_P (°C)		F_{SE} (g/g)		$F_{SP}(g/g)$	
	Expr.	Scheil	Expr.	Scheil	Expr.	Scheil	Expr.	Scheil	Expr.	Scheil
Alloy 1	623.8	623.0	576.3	574.0	557.6	552.8	0.511	0.538	0.975	0.971
Alloy 2	610.9	613.0	579.0	574.6	557.1	552.7	0.355	0.426	0.972	0.971
Alloy 3	620.3	619.0	576.9	574.2	556.2	552.9	0.453	0.498	0.971	0.970
Alloy 4	618.3	617.0	576.9	572.8	555.9	554.7	0.425	0.485	0.939	0.943
Alloy 5	618.3	617.0	577.3	573.4	554.5	554.2	0.432	0.481	0.932	0.954
Alloy 6	618.6	617.6	572.8	570.8	556.5	555.4	0.463	0.509	0.905	0.909
Alloy 7	617.1	615.0	578.4	573.7	557.7	554.0	0.414	0.460	0.955	0.957
Alloy 8	625.1	625.0	577.6	573.9	553.1	552.6	0.516	0.563	0.981	0.972
Alloy 9	617.5	620.0	574.9	574.0	552.7	553.1	0.454	0.507	0.978	0.968
Alloy 10	608.8	609.9	578.9	574.9	556.0	557.9	0.319	0.550	0.977	0.977



Fig. 8—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 1.

$$\Delta H_{13} = f_{\mathrm{Mg}_{2}\mathrm{Si}} \Delta H_{\mathrm{Mg}_{2}\mathrm{Si}} + (1 - f_{\mathrm{Mg}_{2}\mathrm{Si}}) \Delta H_{\mathrm{sludge}}, \quad [12]$$

where ΔH_{Mg_2Si} and ΔH_{sludge} are, respectively, the heat of formation of Mg₂Si and sludge and f_{Mg_2Si} is the mass fraction of Mg₂Si in the total amount of precipitate.

This particular alloy system in which two phases precipitate simultaneously (Mg_2Si and sludge), adds the challenge of determining the relative amount of each phase in the total amount of precipitate. In the present case, this phase balance was determined using the Scheil solidification module of Thermo-Calc software and the

results are listed in Table III. In the case of single-phase precipitates, this previous thermodynamic analysis is not necessary.

Using Thermo-Calc software TTAL7 Al-alloy database v7.1, the heat of formation of Mg₂Si is $\Delta H_{Mg_2Si} = -472.1 \text{ J/g}^{[21]}$ which is calculated from the average of $H_{Mg_2Si} - H_L$ during precipitation of Alloy 6. The heat of formation of sludge is $-47.0 \text{ J/g}^{[21]}$ calculated in a similar manner to Mg₂Si. These value are consistent with the values published in Reference 27. Considering the final mass fractions of Mg₂Si and sludge based on Scheil model for solidification, ΔH_{13}



Fig. 9-Precipitate fraction vs temperature forming in Alloy 1 during solidification.



Fig. 10-Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 2.

was calculated to be in the range of -130.2 to -207.0 J/g for all the alloys presented in Table II.

IV. RESULTS

Ten different alloys of compositions listed in Table II were studied to compare the methodology presented with computational thermodynamic analysis. For all ten alloys the evolution of phase fraction for solid aluminum and precipitates was determined with both techniques. In this section, general details of results are discussed using Alloy 6 as an example.

Figure 5 uses Alloy 6 to compare the results from the current methodology to both equilibrium and Scheil model for solidification obtained using Thermo-Calc. The formation of primary aluminum dendrites, eutectic, and precipitates are clearly marked on this graph. Similarly, the $\{Mg_2Si + Al_8FeMg_3Si_6\}$ precipitate fraction for Alloy 6 is displayed in Figure 6. The precipitation of the sludge and Mg_2Si are also shown in Figure 6. It is worth mentioning that the solid aluminum fraction in Figure 5 does not reach 1 due to the



Fig. 11-Precipitate fraction vs temperature forming in Alloy 2 during solidification.



Fig. 12—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 3.

formation of precipitates. For this specific alloy (Alloy 6), the final phase fraction consists of 0.9836 solid aluminum and 0.0164 precipitates.

Alloy 6 was chosen as an example due to the high fraction of precipitates which form during solidification. The final fraction of precipitates in the aluminum samples calculated by the presented method is displayed in Table III. This table also includes the final equilibrium precipitate fraction and that predicted by Scheil model of solidification. The final mass fraction of Mg₂Si and the heat of formation of the precipitates are also given in Table III. To test the accuracy of the methodology presented here, the final precipitate mass fractions

are compared to that obtained from computational analysis for all ten alloys in Figure 4. This figure demonstrates the power of the proposed methodology in producing accurate results.

The phase fraction evolution curves contain valuable information regarding the transformation start/finish temperatures and the amount of each phase at these specific temperatures. Figure 7 schematically displays the most important information obtained from a phase fraction curve which includes the liquidus temperature, eutectic temperature and solid fraction at this temperature, precipitation temperature and solid fraction at



Fig. 13-Precipitate fraction vs temperature forming in Alloy 3 during solidification.



Fig. 14—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 4.

this temperature. Table IV summarizes the information obtained from the phase fraction curves (curves presented in Figures 5 and 6) for all the alloys (Figure 7).

V. DISCUSSION

The proposed methodology in this paper enables, for the first time, the accurate calculation of phase fractions using cooling curve analysis with multiple simultaneous phase transformations. This methodology overcomes the shortcomings of previous calorimetry approaches of assigning a single enthalpy to all transformations present.

The proposed approach involves a modest amount of effort (*e.g.*, calculating/finding the latent heat of some phases) that is not necessary in previous methodologies; however, this extra effort allows for the proper accounting of phase fractions that is not possible otherwise. With the latest advancements in thermodynamic databases available through commercial software such as Thermo-Calc Software, the amount of resources spent on gathering the extra information required for this methodology is relatively small. In addition, the effort



Fig. 15-Precipitate fraction vs temperature forming in Alloy 4 during solidification.



Fig. 16-Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 5.

spent on analyzing a specific alloy group does not need to be repeated for similar systems; therefore, the analysis of experimental curves does not need independent Thermo-Calc runs for each analysis once the enthalpy of precipitates is known. By measuring the final precipitate fraction in unknown systems or systems which do not have reliable thermodynamic databases available, the enthalpies of all phase transformations involved can be accurately back-calculated. This is an advantage over relying solely on available thermodynamic databases and can be used to get a deeper understanding of new or custom alloy systems. The phase evolution and final amount of phases correspond well to those calculated using Thermo-Calc software. The maximum deviation in the amount of precipitate is an overestimate of 7.1 pct (for Alloy 1). Higher accuracy might have been possible if direct measurements of all alloying elements was available.

It is worth mentioning that using aluminum A356 alloy as an example in this paper also plays a role in the accuracy of the calculated precipitate fraction. The magnitude of the latent heat of formation of the precipitates is large enough to be able to track their evolution during solidification $(\Delta H_{solidification})$ is comparable to $\Delta H_{precipitation})$.



Fig. 17—Precipitate fraction vs temperature forming in Alloy 5 during solidification.



Fig. 18-Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 6.

The developed methodology can be used as a complimentary method to well-established methods curto track rently being used multiple phase transformations (e.g., dilatometry) without having to change the experimental setup. In fact, by making some minor adjustments to the proposed methodology (Eq. [1]), one can take into account complex heat transfer situations where convection and radiation might coexist (such as high temperature phase transformations in a dilatometry sample). By combining CCA with other experimental techniques, new unexplored and interesting doors in the world of materials science can be opened.

VI. CONCLUSIONS

A rigorous mathematical model for the quantification of simultaneous phase transformations in cooling curve analysis was introduced for the first time. The methodology proposed is based on the integration of cooling curves and knowledge of latent heat and specific heat of phases involved. The outcome of this methodology is an accurate accounting of multiple phase fractions as the transformations progress in continuous cooling and start/finish temperatures during cooling containing multiple simultaneous phase transformations.



Fig. 19—Precipitate fraction vs temperature forming in Alloy 6 during solidification.



Fig. 20-Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 7.



Fig. 21—Precipitate fraction vs temperature forming in Alloy 7 during solidification.



Fig. 22—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 8.

The simultaneous solidification-precipitation of ten variations of aluminum A356 with magnesium and silicon content respectively ranging from 0.13 to 0.69 wt pct and 6.09 to 8.09 wt pct were analyzed using the methodology proposed. The results were in good agreement with values obtained based on the Scheil model of solidification implemented in Thermo-Calc Software TTAL7 Al-alloys database v7.1. The maximum deviation in the amount of precipitate is an overestimate of 7.1 pct (for Alloy 1).

The results of these examples support the presented simultaneous phase transformation methodology as a

tool capable of tracking multiple simultaneous phase transformations and amount of each phase present in the material.

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Fig. 23—Precipitate fraction vs temperature forming in Alloy 8 during solidification.



Fig. 24-Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 9.

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APPENDIX: EVOLUTION OF SOLID ALUMINUM FRACTION AND PRECIPITATE FRACTION WITH TEMPERATURE FOR ALL TEN ALLOYS STUDIED

The developed methodology was used to study the simultaneous solidification-precipitation of all the alloys mentioned in Table II. Thermo-Calc Software was used to predict the equilibrium phase fractions in each of the alloys. Scheil model for solidification was also used in Thermo-Calc Software to predict the phase fractions under non-equilibrium solidification for every alloy.

The resulting phase fraction curves consisting of a solid aluminum fraction curve and a precipitate fraction curve for each of the alloys are shown in the following figures (Figures 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26 and 27). The data used to plot these curves is also used to extract all the important information during the simultaneous solidification–precipitation for each of the alloys.



Fig. 25—Precipitate fraction vs temperature forming in Alloy 9 during solidification.



Fig. 26—Solid aluminum fraction vs temperature for the aluminum matrix forming in Alloy 10.



Fig. 27-Precipitate fraction vs temperature forming in Alloy 10 during solidification.

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