# Numerical analysis of liquid fraction in solid–liquid phase transformation of semisolid alloy

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The non-linear mathematical expression of liquid fraction in solid–liquid phase transformation of semisolid alloy was derived by thermodynamic equations, and the numerical solution of the non-linear mathematical expression was obtained by the Gauss Newton iteration algorithm. The solid–liquid phase transformation of hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg alloy was studied by differential scanning calorimetry, and it was used for the expression reliability validation and compared with the Scheil linear regression expression. The results showed that the liquid fraction of the semisolid alloy was not increased linearly with the heating temperature increasing, but increased non-linearly, which was not consistent with the Scheil expression, and the growth rate of liquid fraction was not entirely the same in different temperature ranges. The non-linear mathematical expression data fit well with the experimental data, and the non-linear mathematical expression had a smaller discrete degree and higher credibility compared with the Scheil linear regression expression. The relationship of liquid fraction and heating temperature of the semisolid alloy can be reflected by means of the non-linear mathematical expression in the case of solid–liquid phase transformation.

**Keywords:** Semisolid processing, Liquid fraction, Non-linear mathematical expression, Thermodynamics, Numerical analysis

## Introduction

In the process of semisolid slurry preparation, keeping adequate liquid fraction $f_L$ is the significant step of semisolid forming technology.[1] The liquid fraction of semisolid slurry is important not only to the quality of semisolid slurry but also to the rheology and thixotropy of semisolid processing.[2,3] At present, liquid fraction of semisolid slurry is basically measured by electric resistance measurement, thermal analysis [differential scanning calorimetry (DSC)] and optical image observation.[4] The solid fraction of 7075Al alloy was studied by Lu.[5] It showed that the results of above methods were similar to the results of the experiment. The solid–liquid phase transformation of semisolid alloys is of complex and a non-linear problem for there are solid–liquid interface front end that varied with time. Only simple questions can obtain analytical solutions. The majority of the cases are solved by numerical methods, which are very important means to deal with this kind of problems.[6] The liquid fraction expressions of semisolid slurry in the published literatures were mainly deduced by equilibrium phase diagram of the alloy or obtained by numerical fitting, such as the famous Scheil expression,[7] which was derived by diffusion theory for single phase alloy solidification, under the assumption that the solute equilibrium partition coefficient was a constant, and solidus and liquidus were straight lines. According to Scheil expression, there was linear relationship between liquid fraction and temperature. Luo and Zhang[8] proposed a computational method of solid fraction of Mg–40Pb semisolid alloy, and the liquidus and solidus of the alloy were parabola fitted first, and then the solid fraction of the alloy was solved by the lever rule. Al–5·8Cu binary alloy in the process of melting was studied by Wang.[2] The relationship between liquid fraction and temperature was given by introducing $\beta$ (diffusion parameter) parameter, which actually expanded the Scheil expression.

Those researches mentioned above were based on the melting and solidification process of single phase or binary alloy. The transformation laws of liquid fraction in their scope of application can be accurately illustrated, which played an important theoretical guiding role in liquid fraction research. However, those expressions could not meet the requirements of practical applications because they had lower precision to calculate the liquid fraction of multiphase semisolid alloys.[8] In this paper, the non-linear mathematical expression of liquid fraction in solid–liquid phase transformation of semisolid alloy was derived by thermodynamic equations in the macroscopic point of view, and the numerical solution of the non-linear mathematical expression was obtained by the Gauss Newton iteration algorithm. The solid–liquid phase transformation of hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg alloy was studied by DSC, and it was used for the expression reliability validation. The results

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showed that the non-linear mathematical expression had a higher credibility compared with the Scheil linear regression expression, and it can be used to calculate the liquid fraction of semisolid alloys more accurately.

## Establishment of mathematical expression and its solution

The calculation of liquid fraction is essentially the melting or solidification process controlling of the semisolid alloys. The factors of semisolid alloy melting or solidification process are the thermal equilibrium condition, the change of morphology and composition of each phase. The solute diffusion has varying effects on melting and solidification of semisolid alloy.[2] Therefore, it is very difficult to calculate liquid fraction of semisolid slurry precisely. It is conducive to solve the problem with the method of thermodynamics, which analyse the process of solid–liquid phase transformation of semisolid alloy from the view of the macroscopic properties and macroscopic phenomena without considering the effect of the microstructure and movement of various phases on it.[9] According to the thermodynamics analysis, Gibbs free energy $G$ can be expressed as a function of temperature $T$ and composition $C$ for multiphase of semisolid alloy at constant pressure[2]

$$G=f(T,C) \tag{1}$$

Near equilibrium melting in slow heating rate can be regarded as thermodynamic equilibrium state. The solid and liquid phase in the thermodynamic equilibrium state has the same free energy. Thus, for a given composition of alloy, the liquid fraction of semisolid slurry is determined by semisolid processing temperature. In the heating process, diffusion plays an important role in the alloy microstructure with the change of temperature and the chemical potential. The disorder phenomenon and complexity of alloy, which are caused by solute diffusion with composition change, can be characterised by entropy $S$. In the melting process, if the solute in the liquid phase is completely diffused, namely, liquid composition is equal, according to the equilibrium principle of interface area, the alloy melting is the result that combined with temperature and composition. The finish of alloy melting process is only related with the heating temperature instead of the other parameters, such as heating rate.

According to the thermodynamics analysis above, it was necessary to do some reasonable simplification and assumption before establishing the mathematical expression:

(i) the alloy is isotropic
(ii) the microstructure of the alloy is uniform and it had no segregation based on isotropic
(iii) in constant pressure heating process, the constant volume closed system can be considered as the thermodynamic equilibrium state.[9]

Irrespective of the dynamic overheating caused by non-equilibrium of the solid–liquid interface under the condition of rapid melting, and irrespective of the thermodynamic overheating caused by low energy interface that exists in the low dimension materials, the liquid phase is the result of alloy meeting the thermodynamic conditions of equilibrium melting. The driving force of liquid–solid diffusion is chemical potential gradient without considering the interaction between alloy elements,[2] since the solute diffusion in the solid phase is far less than the liquid phase.

Based on the simplification and assumption above, the thermodynamics of the alloy of the unit mass can be expressed as the following equation[9]

$$\mathrm{d}H=T\mathrm{d}S \tag{2}$$

For closed system

$$\mathrm{d}H=C_\mathrm{P}\mathrm{d}T \tag{3}$$

where $C_\mathrm{P}$ is average constant pressure heat capacity (J °C$^{-1}$ g$^{-1}$), $T$ is heating temperature (°C) and $H$ is enthalpy. Since $\Delta S=\Delta H/T$

$$C_\mathrm{P}\Delta T=T\Delta S \tag{4}$$

where $\Delta T=T-T_\mathrm{m}$, $T_\mathrm{m}$ is the melting point of the alloy (°C). Suppose the chemical potentials of one alloy element $i$ in liquid and solid phase ($\mu_\mathrm{i}^\mathrm{L}$,$\mu_\mathrm{i}^\mathrm{S}$) are as follows[10]

$$\mu_\mathrm{i}^\mathrm{L}=\mu_{0\mathrm{i}}^\mathrm{L}(T)+RT\ \ln(1-x_\mathrm{i}^\mathrm{L}) \tag{5}$$

$$\mu_\mathrm{i}^\mathrm{S}=\mu_{0\mathrm{i}}^\mathrm{S}(T)+RT\ \ln(1-x_\mathrm{i}^\mathrm{S}) \tag{6}$$

where $\mu_{0\mathrm{i}}^\mathrm{L}(T)$ and $\mu_{0\mathrm{i}}^\mathrm{S}(T)$ are standard chemical potentials of the element $i$ in liquid and solid phase respectively; $x_\mathrm{i}^\mathrm{L}$ and $x_\mathrm{i}^\mathrm{S}$ are mole fractions of the solute of the element $i$ in liquid and solid phase respectively; and $R$ is the gas constant. Under different temperatures, the difference of chemical potentials of the element $i$ is

$$\Delta G=\mu_{0\mathrm{i}}^\mathrm{L}-\mu_{0\mathrm{i}}^\mathrm{L}(T) \tag{7}$$

where $\mu_{0\mathrm{i}}^\mathrm{L}$ is the standard chemical potential of the element $i$ in $T_\mathrm{m}$. When in the condition of constant pressure, there is $\Delta G=-S_\mathrm{i}^\mathrm{L}\Delta T$. Put this equation and equation (7) in equation (5)

$$\mu_\mathrm{i}^\mathrm{L}=\mu_{0\mathrm{i}}^\mathrm{L}+S_\mathrm{i}^\mathrm{L}\Delta T+RT\ \ln(1-x_\mathrm{i}^\mathrm{L}) \tag{8}$$

In the same way,

$$\mu_\mathrm{i}^\mathrm{S}=\mu_{0\mathrm{i}}^\mathrm{S}+S_\mathrm{i}^\mathrm{S}\Delta T+RT\ \ln(1-x_\mathrm{i}^\mathrm{S}) \tag{9}$$

Since the standard chemical potentials of the element $i$ at the $T_\mathrm{m}$ are equal, namely, $\mu_{0\mathrm{i}}^\mathrm{L}=\mu_{0\mathrm{i}}^\mathrm{S}$, and there is $\mu_\mathrm{i}^\mathrm{L}=\mu_\mathrm{i}^\mathrm{S}$ when liquid and solid are phase equilibrium, thus

$$(S_\mathrm{i}^\mathrm{L}-S_\mathrm{i}^\mathrm{S})\Delta T=RT\ \ln\left(\frac{1-x_\mathrm{i}^\mathrm{S}}{1-x_\mathrm{i}^\mathrm{L}}\right) \tag{10}$$

So there is

$$-\Delta S_\mathrm{i}\Delta T=RT\ \ln\left(\frac{1-x_\mathrm{i}^\mathrm{S}}{1-x_\mathrm{i}^\mathrm{L}}\right) \tag{11}$$

Combine equations (4) and (11)

$$\frac{1-x_\mathrm{i}^\mathrm{L}}{1-x_\mathrm{i}^\mathrm{S}}=e^{\frac{\Delta T^2}{RT^2}C_\mathrm{P}}=e^{\frac{(T-T_\mathrm{M})^2}{RT^2}C_\mathrm{P}} \tag{12}$$

Since $k_0^\mathrm{i}=\left(x_\mathrm{i}^\mathrm{S}/x_\mathrm{i}^\mathrm{L}\right)(1/F)$, there is $x_\mathrm{i}^\mathrm{S}=k_0^\mathrm{i}Fx_\mathrm{i}^\mathrm{L}$. Put it in equation (12)

$$x_i^L = \frac{e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1}{k_0^i F e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1} \qquad (13)$$

Equation (13) is the expression of liquid mole fraction of the element *i*, where $k_0^i$ is the solute equilibrium partition coefficient of the element *i*, $F=\left[(C_1^L/A_1)+(C_2^L/A_2)+\cdots+(C_i^L/A_i)\right]/\left[(C_1^S/A_1)+(C_2^S/A_2)+\cdots+(C_i^S/A_i)\right]$, where $C_i^L$ is the concentration of the element *i* in liquid phase, $C_i^S$ is the concentration of the element *i* in solid phase, and $A_1$, $A_2 \ldots A_i$ is the relative atomic mass of element 1,2…*i*. If liquid phase is composed of many elements, such as the total element quantity was *n*, then the total mass fraction in liquid phase $f_L$ is

$$f_L = \sum_{i=1}^{n} f_i^L = \sum_{i=1}^{n} x_i^L A_i = \sum_{i=1}^{n} \frac{e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1}{k_0^i F e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1} A_i \qquad (14)$$

According to the derivation above, equation (14) can be used to calculate the liquid fraction of semisolid alloy in the condition of obtaining thermodynamic data and physical parameters correctly. However, it is very hard and unnecessary to obtain all the precise data. Thus, equation (14) can be simplified, and it can be used to calculate liquid fraction $f_L$ within the permitted error range to meet the actual requirement. For the certain semisolid alloys, according to the thermodynamics analysis, the liquid fraction of alloy slurry is determined by semisolid heating temperature. The liquid fraction $f_L$ can be considered as a function of heating temperature *T* in the actual melting process of alloy. Therefore, it is enable to make $k_0^1 = k_0^2 = \cdots = k_0^i = \cdots = k_0$, $k_0$ constant. For the same, $C_P$ and *F* are also constants. Equation (14) can be simplified as

$$f_L \approx \frac{e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1}{k_0 F e^{\frac{(T-T_M)^2}{RT^2}C_P} - 1} \sum_{i=1}^{n} A_i = \frac{e^{\frac{(T-T_M)^2}{T^2}P_3} - 1}{P_2 e^{\frac{(T-T_M)^2}{T^2}P_3} - 1} P_1 \qquad (15)$$

where $P_1 = \sum_{i=1}^{n} A_i$, $P_2 = k_0 F$, $P_3 = C_P/R$. They are all parameters. Equation (15) is a non-linear function, and it can be numerically analysed by the Gauss Newton iteration algorithm.[11,12] Supposing the non-linear regression expression is

$$f_L = f(T, P) + \varepsilon \qquad (16)$$

where $T=(T_1, T_2, \cdots, T_n)$ is the dependent variable, $P=(P_1, P_2, P_3)$ is the regression parameter and $\varepsilon$ is the error. The solution steps of equation (16) are, first, initial value $P^0$ is given, and the matrix can be calculated. Then, the iteration value $P^*$ can be calculated and used to replace $P^0$ as a new iteration initial value. The steps above should be repeated until the iteration value front and back of $P^*$ is less than the initial given precision.

In order to investigate the precision of the expression that is derived in this paper, the relationship between liquid fraction $f_L$ and heating temperature *T* of hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg is studied by DSC. The DSC experimental data are used for the expression reliability validation, which is obtained by non-linear regression fitting and compared with the linear regression expression that is obtained by the Scheil regression fitting.

## Experimental materials and methods

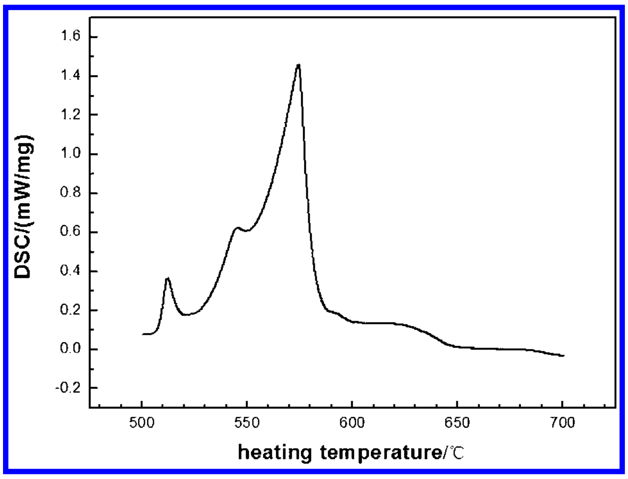
The raw materials used in the test were 99·95 wt-% industrial pure Al, 99·9% pure Cu, 99·98% pure Mg and master alloys of Al–26Si, Al–20Fe and Al–10Mn. The modificator in the test was phosphor copper, and hexachloroethane was used as the refining agent. The chemical composition of the alloy is Al–20Si–3Fe–1Mn–4Cu–1Mg (wt-%).

Hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg was smelted by well resistance furnace, and semisolid slurry was prepared by the self-made electromagnetic stirring device. The sample mass was 8·5±0·2 mg in DSC experiment, and the sample was washed by ultrasonics. The DSC model number was Netzsch DSC 404C (power compensation). The heating temperature rose from room temperature to 700°C at temperature ramp of 10°C $min^{-1}$. Argon was used as protecting gas in the whole experiment process in order to prevent the oxidation of the alloy. The flowrate of argon was 30 mL $min^{-1}$.

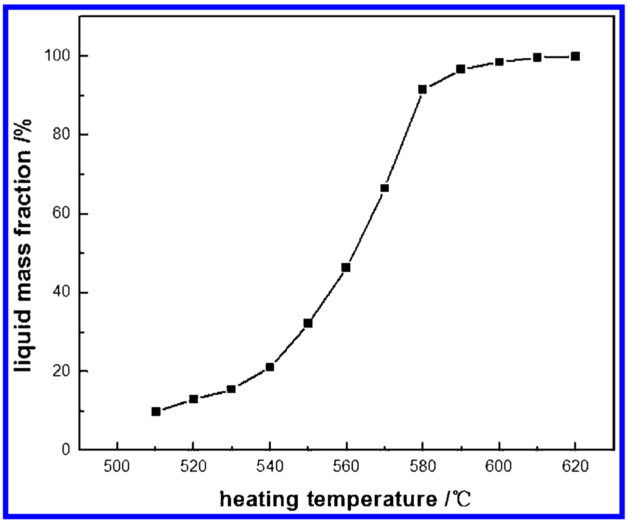
## Experiment results and verification of mathematical expression

The heating DSC curve of hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg was shown in Fig. 1. It can be seen from the figure that the DSC curve had three obvious endothermic peaks. The first sharp endothermic peak came out at 512·4°C, the second at 545·2°C, and the third at 575°C. The second and the third endothermic peaks almost overlapped. It caused the second endothermic peak to incline to a platform more than a peak. The third endothermic peak was sharper on the right side than on the left side, and it had the greatest melting heat. The solidification temperature $T_m$ (507°C) and completely melting temperature $T_L$ (627°C) can be determined by extrapolation method.[2]

The fusion quality of alloy can be acquired by the absorbed heat of fusion due to the constant heating rate in the experiment.[13] Kim *et al.*[14–16] thought that enthalpy variation was directly proportional to the area surrounded by DSC curves and baseline, namely, $\Delta H_T = KA$ [$A$ ($mm^2$) was the area surrounded by DSC curves and baseline; $K$ (J g $mm^{-2}$) was the instrumental constant, and it can be treated as a constant in the




**1 Differential scanning calorimetry curve of semisolid Al–20Si–3Fe–1Mn–4Cu–1Mg alloy**




**2 Relationship between liquid mass fraction and heating temperature of semisolid Al–20Si–3Fe–1Mn–4Cu–1Mg alloy**

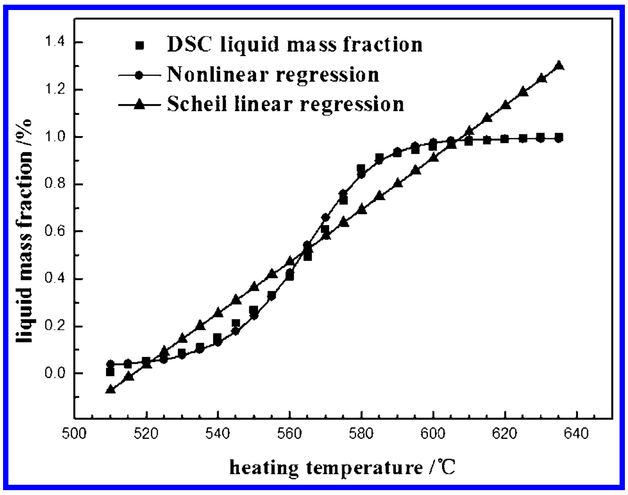
temperature range of the test]. Therefore, the liquid fraction can be determined by the area ratio of the area surrounded by DSC curves and baseline. The liquid fraction of alloy can be obtained from the following equation under a certain temperature $T$

$$f_L = \frac{\Delta H_T}{\Delta H} \tag{17}$$

where $\Delta H_T$ was the enthalpy variation from the start of melting to the temperature $T$ and $\Delta H$ was the enthalpy variation of complete melting. Referring to the method of Kim *et al.*, the relationship between liquid fraction $f_L$ and heating temperature $T$ can be obtained by area integral, as shown in Fig. 2.

As seen in Fig. 2, the liquid fraction of semisolid Al–20Si–3Fe–1Mn–4Cu–1Mg alloy had a tendency to increase with temperature rise. It meets with the Scheil expression. However, the liquid fraction increased in different ways compared with the Scheil expression. The liquid fraction increased from 0·74 to 26·6%, while the temperature increased from 510 to 550°C, and it was relatively flat curve in the temperature range. This was caused by lower melting rate of solid under relatively lower temperature. Between 550 and 580°C, the melting rate of solid was obviously faster, the liquid fraction increased to 88·8% at 580°C, and the curve was increased sharply in the temperature range. After 580°C, the growth rate of liquid fraction was obviously decreased because most of the alloy was melted. The curve increased slowly until the alloy was completely melting. It can be seen that the relationship of liquid fraction and heating temperature was not a simple linear increase as the Scheil expression described but non-linear increased with temperature rise. The growth rate of liquid fraction was not entirely consistent in different temperature range, and the curve was S shaped.

For the non-linear mathematical expression of liquid fraction established in this study, the results of numerical analysis were $P_1=0{\cdot}20737$, $P_2=-16{\cdot}29414$, $P_3=-286{\cdot}05777$, $\varepsilon=-0{\cdot}00671$. Namely, for semisolid Al–20Si–3Fe–1Mn–4Cu–1Mg alloy, the non-linear mathematical expression of liquid fraction $f_L$ was




**3 Comparison of non-linear regression and Scheil linear regression fitting curve with test data**

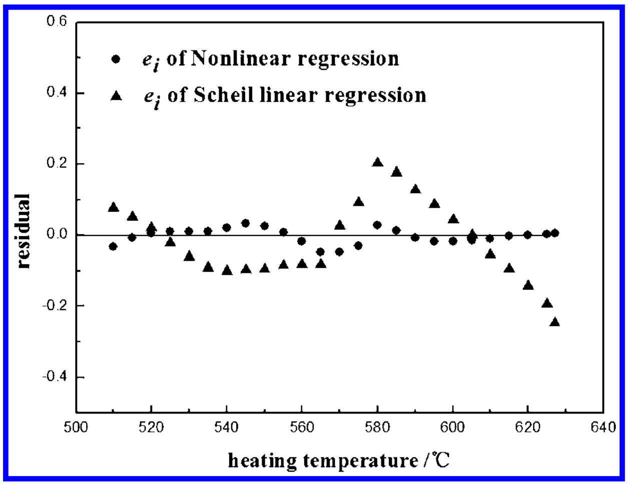
$$f_L = \frac{0{\cdot}20737\left(e^{\frac{-286{\cdot}05777(T-507)^2}{T^2}}-1\right)}{-16{\cdot}29414e^{\frac{-286{\cdot}05777(T-507)^2}{T^2}}-1} - 0{\cdot}0067 \tag{18}$$

For comparison, the Scheil linear expression, which was obtained by linear regression fitting, was

$$f_L = 1{\cdot}31215\left(\frac{T-507}{120}\right)^{1{\cdot}0109} - 0{\cdot}09974 \tag{19}$$

The comparison result of non-linear regression fitting and Scheil linear regression fitting curves with the experimental test is shown in Fig. 3. As seen in Fig. 3,the non-linear mathematical expression data fit well with the experimental data, and it had a smaller discrete degree compared with the Scheil linear regression expression. The relationship of liquid fraction and heating temperature of the semisolid alloy can be reflected in the case of solid–liquid phase transformation.

The residual error $e_i$ of the non-linear regression and Scheil linear regression is shown in Fig. 4. As seen in Fig. 4, the absolute values of these regression residual errors were small, and they were randomly distributed above and under the transverse line. The majority of the values distributed in horizontal strip interval of (0·2,




**4 Comparison of residual error of non-linear regression and Scheil linear regression**

+0·2), that is to say that these regression equations fit well on the sample data. The residual error of non-linear regression was much less than that of the Scheil linear regression, and the coefficient of association $R^2$ of non-linear regression was $R^2$=0·99687, which was superior to the coefficient of association of the Scheil linear regression that was $R^2$=0·9344. It was shown that the non-linear regression expression in this paper had a higher credibility than the Scheil linear expression.

## Conclusions

1. The relationship of liquid fraction and heating temperature of hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg alloy was obtained by DSC. It was shown that the liquid fraction of the semisolid alloy was increased with heating temperature; however, the relationship was not a simple linear one as Scheil expression described but a non-linear one. The growth rate of liquid fraction was not a constant in different temperature ranges, and the growth rate curve was S shaped.

2. The non-linear mathematical expression of liquid fraction in solid–liquid phase transformation of semi-solid alloy was derived by thermodynamic equations, and the numerical solution of the non-linear mathematical expression was acquired by the Gauss Newton iteration algorithm. The research of solid–liquid phase transformation in hypereutectic Al–20Si–3Fe–1Mn–4Cu–1Mg alloy showed that the non-linear mathematical expression data fit well with the experiment data, and the non-linear mathematical expression had a smaller discrete degree and higher credibility compared with the Scheil linear regression expression. The relationship of liquid fraction and heating temperature of the semisolid alloy can be reflected in the case of solid–liquid phase transformation.

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