

Calculation of Phase Equilibria Based on the Levenberg-Marquardt Method

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The Levenberg-Marquardt method, the best algorithm to obtain the least-square solution of nonlinear equations, is applied to calculate the stable phase equilibria. It can get the best combination between robustness and speed of the calculations. Its application to ternary Al-Si-Mg system is executed in detail. The calculated phase equilibria agree well with the experimental results. Furthermore, the Levenberg-Marquardt method is not sensitive to the initial values.

KEY WORDS: Levenberg-Marquardt method; Phase equilibria calculation; Least-square solution

1. Introduction

Computer calculation of phase diagrams began nearly 40 years ago^[1,2]. The history of CALPHAD is a chronology of what can be achieved in the field of phase equilibria by combining basic thermodynamic principles with mathematical formulations to describe the various thermodynamic properties of phases. Up to now, many procedures have been published to calculate the phase diagrams. But most of them are based on the two general ways^[3]: the local minimization methods and the global optimizations methods.

If codes are based on local minimization methods, such as steepest descent or Newton-Raphson, problems will arise due to the existence of unknown local minima in Gibbs energy space. So, more computer codes based on global minimization methods, such as Thermo-Calc^[4], FACT^[5], MTDATA^[6], *etc.*, were designed, but these must sample a large portion of Gibbs energy space so that all of the local minima are recognized. Unfortunately, computational times can then be greatly increased.

Recently, a new method for the calculation of stable phase diagram was presented by Li *et al.*^[7], which can obtain the phase equilibria by minimizing the total deviation of the phase equilibrium equations. He still used the Newton-Raphson method or the simplex method to solve the nonlinear equations of n variables. In this paper, the objective function of phase equilibrium is solved using the well-developed Levenberg-Marquardt method^[8], which can get the best combination between robustness and speed of the calculation.

2. Objective Function of the Calculation

For all solution phases, the Gibbs energy can be given by the general formula^[9]:

$$G = G^0 + G_{\text{mix}}^{\text{ideal}} + G_{\text{mix}}^{\text{xs}} \quad (1)$$

where G^0 is the contribution of the pure components of the phase to the Gibbs energy, $G_{\text{mix}}^{\text{ideal}}$ is the ideal mixing contribution and $G_{\text{mix}}^{\text{xs}}$ is the contribution due to non-ideal interactions between the components, also known

as the Gibbs excess energy of mixing.

At a given pressure and temperature, the maximum number of coexisting phases in a system, formed by n components, is equal to $n+1$ as deduced from the phase rule. If a system is formed by m phases, with $1 < m < n+1$, the chemical potential of each component is the same in each phase when equilibrium is reached. This state is expressed by a set of n nonlinear equations:

$$\mu_i^{<1>} = \mu_i^{<2>} = \dots = \mu_i^{<m>} \quad i = 1 \text{ to } n \quad (2)$$

where μ denotes the chemical potential, the superscripts $<1>$, $<2>$, \dots , $<m>$ referring to the different phases and the subscripts i to the component. For a two-phase equilibrium, Eq.(2) then becomes:

$$\mu_i^{<1>} - \mu_i^{<2>} = 0 \quad i = 1 \text{ to } n \quad (3)$$

There are $2n-2$ dependent variables in Eq.(2) considering the mass balance in each phase. To reduce the degrees of freedom to zero, $n-2$ variables must be fixed before the calculation of phase equilibrium. So Eq.(2) contains n variables. Now, let us define the objective function for the phase equilibrium calculation:

$$F(x) = \frac{1}{2} \sum_{i=1}^n f_i^2(x) = \frac{1}{2} f^T f \quad (4)$$

where

$$f_i(x) = \mu_i^\alpha - \mu_i^\beta = 0 \quad i = 1 \text{ to } n \quad (5)$$

$$x = (x_1, x_2, \dots, x_n) \quad (6)$$

$$f^T = (f_1, f_2, \dots, f_n) \quad (7)$$

The objective function, $F(x)$, cannot be negative. When $F(x)$ is smaller than the reasonably small quantity ε , for example 0.0001, actually it reaches its global minimum^[7]. The condition $F(x) \leq \varepsilon$ corresponding also to the equilibrium condition that the chemical potentials of the different species remain the same in different phases. This can be deduced from the condition that the Gibbs energy of the whole system gets its global minimum. Thus, as soon as $F(x) \leq \varepsilon$, the global minimum of the Gibbs energy in the whole system is reached.

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3. Levenberg-Marquardt Method

Levenberg-Marquardt method is an approximation to Newton's method. The algorithm uses the second-order derivatives of the objective function so that a better convergence behavior is observed. In the ordinary gradient descent search, only the first-order derivatives are evaluated and the parameter change information contains solely the direction along which the objective is minimized, whereas the Levenberg-Marquardt technique extracts a better parameter change vector. It is motivated by this problem that, on the objective surface, there may be many solutions leading to the convergence, raising the possibility of an excessively long time to reach the solution. Using the phase equilibrium equations, the algorithm can be stated as follows:

Suppose $J(x)$ is the Jacobian matrix of $f(x)$, i.e.:

$$J = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix} \quad (8)$$

The gradient matrix of $f(x)$ is:

$$g(x) = \sum_{i=1}^n f_i(x) \nabla f_i(x) = J(x)^T f(x) \quad (9)$$

And the Hessian matrix of $f(x)$ is:

$$G(x) = \sum_{i=1}^n [\nabla f_i(x) \nabla f_i(x)^T + f_i(x) \nabla^2 f_i(x)] = J(x)^T J(x) + S(x) \quad (10)$$

So the Newton algorithm to minimize the objective function can be described as:

$$x_{k+1} = x_k - [J(x_k)^T J(x_k) + S(x_k)]^{-1} J(x_k)^T f(x_k) \quad (11)$$

The Gauss-Newton algorithm can be obtained by neglecting the high order term $S(x)$:

$$x_{k+1} = x_k - [J(x_k)^T J(x_k)]^{-1} J(x_k)^T f(x_k) \quad (12)$$

The Levenberg-Marquardt method is a useful alternative when the Gauss-Newton algorithm yields an ill-conditioned problem and its final form of the parameter update algorithm is described by Eq.(13) and the details are presented in literature [10,11].

$$x_{k+1} = x_k - (J(x_k)^T J(x_k) + \lambda_k I)^{-1} J(x_k)^T f(x_k) \quad (13)$$

4. Robustness and Speed of the L-M Method

For large λ_k , the update formula given by Eq.(13) becomes the standard gradient descent with step size

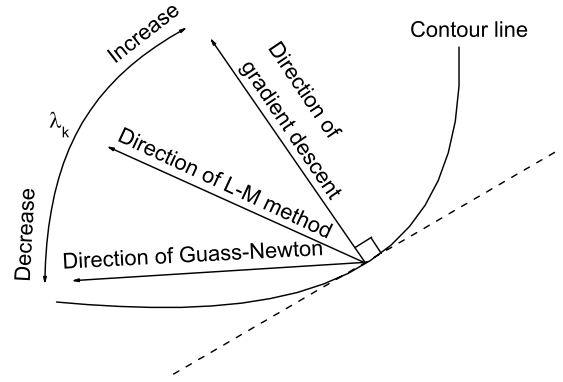


Fig.1 Descent directions of three algorithms

$1/\lambda_k$; conversely for small λ_k , the behavior is as that of Newton's method. Therefore, by the introduction of such a term, a smooth transition between Newton's method and steepest descent is achieved. The descent direction of L-M method is shown in Fig.1. Furthermore, this term introduces the elimination of invertibility problem in Eq.(13).

There must be the flat region and the extremum region in the objective function surface. In the flat region, λ_k should be large in order to get the fastest descent speed. But in extremum region, λ_k should be small in order to eliminate concussive results obtained by gradient descent method and to keep the descent direction. The calculation process is executed in MATLAB and λ_k is determined automatically.

5. Calculation Results

When the chemical potentials are deduced, the objective function $F(x)$ can be written immediately. This method can be used to calculate any two-phase equilibria if we put the corresponding equilibrium condition into the objective function. As an example, the isothermal section containing the liquid and fcc_Al phase in Al rich Al-Mg-Si alloys is calculated in detail using the Levenberg-Marquardt method.

Using the Redlich-Kister-Muggianu model^[12,13], the Gibbs energy of the liquid or the fcc_Al phase can be written as:

$$G = \sum_{i=1}^n x_i^0 G_i^{ref} + RT \sum_{i=1}^n x_i \ln x_i + G^E \quad (14)$$

$$G^E = \sum_{i=1}^2 \sum_{j=i+1}^3 x_i x_j \sum_{l=0}^m [L_{ij,l} (x_i - x_j)^l] + x_1 x_2 x_3 \left[\sum_{i=1}^3 (L_{ter,i} x_i) \right] \quad n = 3 \quad (15)$$

Then, the objective function $F(x)$ can be deduced. The thermodynamic parameters of Al-Mg-Si alloy are selected according to literature [14].

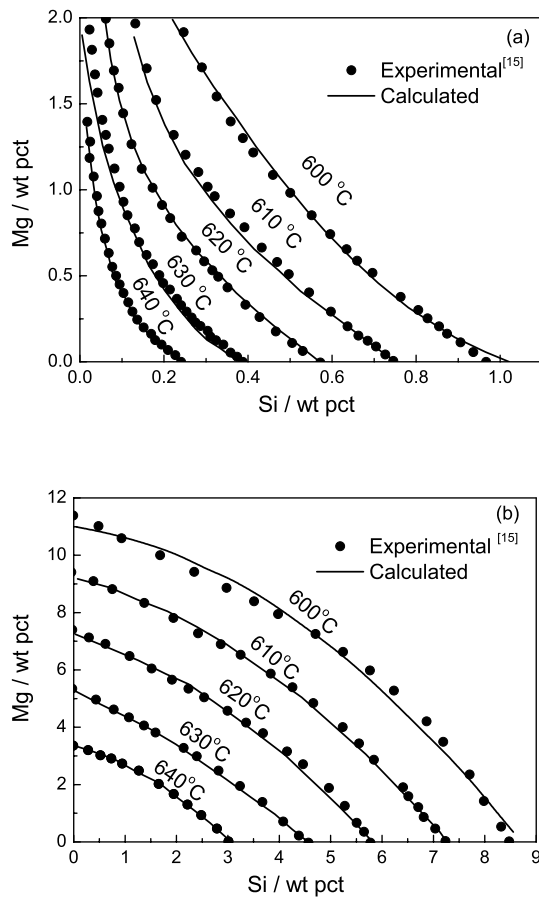


Fig.2 Isothermal sections of Al-Si-Mg alloys, (a) solidus, (b) liquidus

Figure 2 shows a comparison between the calculated values with the experimental results. It can be seen that the calculated values agree well with the experimental results^[15].

6. Conclusion

The Levenberg-Marquardt method, the best algorithm to obtain the least-square solution of nonlinear

equations, is applied to calculate the stable phase diagram. The algorithm uses the second-order derivatives of the objective function so that it can get the best combination between robustness and speed of the calculations. As shown in literature [7], the Meijering's principle^[16] should be applied before the calculation of ternary systems when the miscibility gap exists. This method is suitable for the calculation of the stable equilibria in binary or even higher order alloys.

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