Appendix 4

MATHEMATICAL APPROXIMATION OF PHASE DIAGRAMS

In practice, the most convenient application of multicomponent phase diagrams to the analysis of a specific alloy is the use of polythermal and isothermal sections that enable one to quantitatively determine critical temperatures \( T_i \) and, for ternary systems, the relative mass fractions of the phases \( Q_i \). Not much of such sections are available in the literature and most researchers need to evaluate these sections themselves, using known rules (Zakharov, 1990). However, the correct construction of curved lines requires meticulous processing of primary graphical information (liquidus, solidus, solvus etc.) that, in turn may be not accurate, which degrades the accuracy of \( T_i \) and \( Q_i \) estimation.

Another approach includes the use of thermodynamical calculations. As a result all the surfaces are described analytically, and \( T_i \) and \( Q_i \) can be calculated exactly. Some of the results obtained in such a way are summarized in Appendix 5. However, the software packages based on thermodynamic calculations, e.g. Thermocalc, are specialized and rather expensive. Frequently, the application of such a software is limited by available thermodynamic functions or databases, especially in the case of ternary and quaternary phases.

We suggest some principles and methods of quantitative analysis of multicomponent phase diagrams using a widely available Excel spreadsheet software that allows one to create convenient calculation forms as applicable to a specific problem.

The proposed method is based on the calculation of mass fractions of phases in any \( N \)-phase alloy and the determination of the boundaries of \( N \)-phase regions in \( N \)-component systems. We are using the rule that the compositions of all phases (at a constant temperature) in an \( N \)-phase region of an \( N \)-component phase diagram are constant, irrespective of the alloy composition. The relative mass fractions of the phases can be calculated by solving a system of \( N \) linear balance equations, where the concentration of each alloy component \( (X_i) \) is determined as the sum of products \( Y_{ij}Q_{Mj} \) (where \( Y_{ij} \) is the concentration of the \( i \)-component in the \( j \)-phase and \( Q_{Mj} \) is the mass fraction of the \( j \)-phase):

\[
\begin{align*}
Y_{11}Q_{M1} + Y_{12}Q_{M2} + \cdots + Y_{1N}Q_{MN} &= X_1 \\
Y_{21}Q_{M1} + Y_{22}Q_{M2} + \cdots + Y_{2N}Q_{MN} &= X_2 \\
&\vdots \\
Y_{N1}Q_{M1} + Y_{N2}Q_{M2} + \cdots + Y_{NN}Q_{MN} &= X_N
\end{align*}
\]

(1)
Appendix 4

As only $N-1$ concentrations are independent, and the sum of all mass fractions of $N$ phases equals unity (or 100%), system (1) can be modified as follows:

$$\begin{align*}
Y_{11}Q_{M1} + Y_{12}Q_{M2} + \cdots + Y_{1N}Q_{MN} &= X_1 \\
Y_{21}Q_{M2} + Y_{22}Q_{M2} + \cdots + Y_{2N}Q_{MN} &= X_2 \\
& \vdots \\
Q_{M1} + Q_{M2} + \cdots + Q_{MN} &= 1
\end{align*}$$

(2)

The system of linear equations with $N$ unknowns is usually solved through an $N$-degree determinant, e.g. for system (2) the matrix of principal determinant reads as follows:

$$\Delta = \begin{vmatrix}
Y_{11} & Y_{12} & \cdots & Y_{1N} \\
Y_{21} & Y_{22} & \cdots & Y_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
1 & 1 & \cdots & 1
\end{vmatrix}$$

(3)

Partial determinants $\Delta_1, \Delta_2, \ldots, \Delta_N$ can be obtained by substitution of a column $Y_{ij}$ for free members $(X_1, X_2, \ldots, X_{N-1}, 1)$. After that, the values of $Q_{Mi}$ can be obtained as $Q_{Mi} = \Delta_i / \Delta$.

The volume fractions $Q_{Vi}$, which are very useful for evaluation of many alloy properties, can be calculated using the phase density $\rho_i$:

$$Q_{Vi} = (Q_{Mi}/\rho_i)/(Q_{M1}/\rho_1 + Q_{M2}/\rho_2 + \cdots Q_{MN}/\rho_N)$$

(4)

**Example 1: Ternary system.** Let us consider three-phase equilibria in the aluminum-corner of the Al–Fe–Si system (Section 1.1) (Belov and Matveeva, 2001). Three four-phase solidification reactions involving (Al) occur in the system (Table 1.2), i.e.

$$L + Al_3Fe \Rightarrow (Al) + Al_8Fe_2Si;$$

$$L + Al_8Fe_2Si \Rightarrow (Al) + Al_5FeSi;$$

and

$$L \Rightarrow (Al) + Al_5FeSi + (Si)$$

Correspondingly, the following three three-phase regions are formed in the solid state (Figure 1.1c), i.e.

$$(Al) + Al_3Fe + Al_8Fe_2Si;$$

$$(Al) + Al_8Fe_2Si + Al_5FeSi;$$

and

$$(Al) + Al_5FeSi + (Si)$$
Despite numerous experimental data that are available on this system, the complexity of this phase diagram hinders the analysis of alloy phase compositions without adequate sections. The demand for the efficient analysis of Al–Fe–Si alloys facilitated the development of the calculation procedure described earlier. The following set of balance equations was solved:

\[
\begin{align*}
Q_{M1}C_{Fe1} + Q_{M2}C_{Fe2} + Q_{M3}C_{Fe3} &= C_{FeX} \\
Q_{M1}C_{Si1} + Q_{M2}C_{Si2} + Q_{M3}C_{Si3} &= C_{SiX} \\
Q_{M1}C_{Al1} + Q_{M2}C_{Al2} + Q_{M3}C_{Al3} &= C_{AlX},
\end{align*}
\]

where \(Q_{M1}, Q_{M2},\) and \(Q_{M3}\) are the mass fractions of the respective phases, and \(C_{Fe}, C_{Si}, C_{Al}\) and \(C_{FeX}, C_{SiX}, C_{AlX}\) are the mass concentrations of Fe, Si, and Al in the \(i\)-phase and in the analyzed alloy \(X\), respectively. Evidently, the last equation can be substituted for

\[
Q_{M1} + Q_{M2} + Q_{M3} = 1.
\]

Here we consider the calculation for the phase region \((Al) + Al_6Fe + Al_8Fe_2Si\). By taking into account that \(Al_6Fe\) and \(Al_8Fe_2Si\) have virtually constant composition in the entire temperature range, 20 to 660°C, the calculation of \(Q_{M1}\) requires only the concentrations of iron and silicon in the aluminum solid solution, \(C_{FeAl}\) and \(C_{SiAl}\), respectively. Using data in Table 1.4, one can calculate temperature dependences of \(C_{FeAl}\) and \(C_{SiAl}\). These dependences are introduced in the Excel spreadsheet form. Now, the user fills only tree fields in the form, i.e. the alloy composition (Fe, Si) and temperature (shown in bold in Figure A4.1), and receives the sought parameters \(Q_{M1}\) and \(Q_{V1}\) as an output of calculations. This form allows one to calculate the boundaries of the phase field \((Al) + Al_6Fe + Al_8Fe_2Si\) at any temperature and composition in the solid state, by assigning a zero value to either \(Q_{M1}\) or \(Q_{V1}\) of the phase that disappears at the boundary, i.e. to calculate solvus surfaces. The volume fraction of phases can be calculated provided the values of density are known (Figure A4.1).

Similarly, the calculation forms for other three-phase regions \(-(Al) + Al_8Fe_2Si + Al_5FeSi, (Al) + Al_3FeSi + (Si), L + (Al) + Al_3Fe, L + (Al) + Al_8Fe_2Si, L + (Al) + Al_5FeSi, and L + (Al) + (Si)\) – can be developed.

Such forms can be used for the calculation of invariant reactions (Table 1.2) that allows one to determine the limit points at the horizontal lines of polythermal sections as shown in Figure 1.7. The liquidus polytherms can be constructed using approximating functions derived from liquidus isotherms (Figure 1.1b). The construction of boundaries of single- and two-phase regions requires additional data, but these regions are usually so narrow that their precise position is not practically important.
Construction of isothermal sections like those shown in Figure 1.6 is based on the calculation of canode triangles. If phases have narrow homogeneity ranges and the composition of (Al) is known, then the position of boundaries can be determined quite accurately.

Same forms can be used for the calculation of the dependences of phase volume fractions on the concentration of one of the components (Figure 1.9) or on the temperature. These dependences can be used in the optimization of alloy composition and heat treatment.

And, of course, all these calculations can be embedded in a single file/spreadsheet.

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>(Al)</th>
<th>Al₃Fe</th>
<th>Al₈Fe₂Si</th>
<th>ALLOY</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, %</td>
<td>0.21</td>
<td>0.00</td>
<td>7.00</td>
<td>0.30</td>
<td>550</td>
</tr>
<tr>
<td>Fe, %</td>
<td>0.017</td>
<td>37.00</td>
<td>33.00</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

**RESULT**

\[
\begin{align*}
Q_{M1,\%} &= 94.49 \\
Q_{M2,\%} &= 4.12 \\
Q_{M3,\%} &= 1.39 \\
SUM &= 100.00
\end{align*}
\]

**SUM = 100.00**

Figure A4.1. Excel spreadsheet for calculation of mass \((Q_M)\) and volume \((Q_V)\) fractions of phases in Al–Fe–Si alloys in the \((Al) + Al₃Fe + Al₈Fe₂Si\) phase field.

**Example 2: Quaternary system.** Here we consider the aluminum corner of the Al–Fe–Mg–Si system (Section 2.4) (Belov, 2005). The following four-phase regions exist in this portion of the system in the solid state (Figure 2.4a):

\[
\begin{align*}
(Al) + (Si) + Mg₂Si + Al₈FeMg₃Si₆; \\
(Al) + (Si) + Al₅FeSi + Al₈FeMg₃Si₆; \\
(Al) + Mg₂Si + Al₅FeSi + Al₈FeMg₃Si₆; \\
(Al) + Mg₂Si + Al₅FeSi + Al₈Fe₂Si; \\
(Al) + Mg₂Si + Al₈Fe₂Si + Al₃Fe; \\
(Al) + Mg₂Si + Al₈Fe₂Si + Al₃Fe + Al₈Mg₅
\end{align*}
\]
The composition of all phases, except (Al), is constant. The composition of (Al) can be calculated (by approximating functions) using the data on Al–Mg–Si alloys (Table 2.4) because the solubility of Fe in (Al) is very small.

The following system of four linear equations should be solved in order to calculate the mass fractions of phases:

\[
\begin{align*}
Q_{M1}C_{Si1} + Q_{M2}C_{Si2} + Q_{M3}C_{Si3} + Q_{M4}C_{Si4} &= C_{SiX} \\
Q_{M1}C_{Mg1} + Q_{M2}C_{Mg2} + Q_{M3}C_{Mg3} + Q_{M4}C_{Mg4} &= C_{MgX} \\
Q_{M1}C_{Fe1} + Q_{M2}C_{Fe2} + Q_{M3}C_{Fe3} + Q_{M4}C_{Fe4} &= C_{FeX} \\
Q_{M1} + Q_{M2} + Q_{M3} + Q_{M4} &= 1,
\end{align*}
\]

where \(Q_{M1}, Q_{M2}, Q_{M3},\) and \(Q_{M4}\) are the mass fractions of the respective phases, and \(C_{Si1}, C_{Mg1}, C_{Fe1}\) and \(C_{SiX}, C_{MgX}, C_{FeX}\) are the mass concentrations of Si, Mg, and Fe in the \(i\)-phase and the analyzed alloy \(X\), respectively.

Figure A4.2 shows the spreadsheet form for the phase region (Al)+(Si)+Mg\(_2\)Si+Al\(_5\)FeMg\(_3\)Si\(_6\). The negative volume fraction (in this case – Mg\(_2\)Si) means that the equilibrium alloy at this particular temperature does not fall into the four-phase region containing this phase. The dependences of the volume fractions of individual phases on the concentration of an alloying element can reveal some tendencies that cannot be found without such a calculation, see Figure 2.8 as an example.

Let us look in more detail at the construction of a polythermal section of this system at 7% Si and 0.2% Fe as shown in Figure 2.13a. The liquidus polytherm for the primary solidification of (Al) can be calculated using data on the liquidus isotherms of the constituent ternary systems. Similarly, one can calculate the polytherm for the solidification of the binary \(L\Rightarrow\text{(Al)+(Si)}\) eutectics that occurs in all alloys of the given polythermal section. Then the calculation shows that two invariant horizontals should be present in the considered compositional range, one for the eutectic reaction \(L \Rightarrow \text{(Al)+(Si)+Mg}_2\text{Si+Al}_5\text{FeMg}_3\text{Si}_6\) at 554°C and the other the peritectic reaction \(L + \text{Al}_5\text{FeSi} \Rightarrow \text{(Al)+(Si)+Al}_5\text{FeMg}_3\text{Si}_6\) at 567°C (Table 2.8). The points at these horizontals from which the lines bordering the three- and four-phase regions start can also be determined. The calculation of these phase fields at different temperatures allows one to draw their borders.

Isothermal sections at 7% Si shown in Figure 2.12 are constructed based on the calculation of canode tetrahedrons. As the boundaries of four-phase fields in the isothermal plane should appear as straight lines, their position can be determined by two points.

In the case of 6XXX-series alloys, the phase field boundaries are so close to each other that only calculation allows one to distinguish these boundaries (see Figure 2.7).
Appendix 4

System Al–Fe–Si–Mg (Al) + Al$_8$Fe + Mg$_2$Si + Al$_8$FeMg$_3$Si$_6$

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>(Al)</th>
<th>(Si)</th>
<th>Mg$_2$Si</th>
<th>Al$_8$FeMg$_3$Si$_6$</th>
<th>ALLOY</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, %</td>
<td>0.11</td>
<td>99.5</td>
<td>36.7</td>
<td>32.9</td>
<td>7</td>
<td>200</td>
</tr>
<tr>
<td>Mg, %</td>
<td>0.05</td>
<td>0</td>
<td>63.2</td>
<td>14.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Fe, %</td>
<td>0.01</td>
<td>0</td>
<td>1</td>
<td>10.9</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RESULT

Q$_M$, wt%  Q$_V$, vol.%

(Al) 90.38 89.97
(Si) 5.72 6.60
Mg$_2$Si $-0.60$ $-0.86$
Al$_8$FeMg$_3$Si$_6$ 4.50 4.29
SUM 100 100

Phase density, g/cm$^3$

(Al) 2.7
(Si) 2.33
Mg$_2$Si 1.88
Al$_8$FeMg$_3$Si$_6$ 2.82

Figure A4.2. Excel spreadsheet for calculation of mass (Q$_M$) and volume (Q$_V$) fractions of phases in Al–Fe–Mg–Si alloys in the (Al) + (Si) + Mg$_2$Si + Al$_8$FeMg$_3$Si$_6$ phase field.

Example 3: Quinary system. The algorithm considered here for ternary and quaternary systems does not change much on transition to more complex systems. Moreover, the calculation of multicomponent phase diagram is, in many cases, the only way to extract the required information.

Take as an example the Al–Cu–Fe–Mg–Si system (Section 3.7) in the range of Al–Si alloys. The distribution of phase fields in the solid state of this system is shown in Figure 3.8a. By taking into account that the compositions of excess phases are constant, and the composition of (Al), due to a small solubility of iron, can be calculated from the data on the Al–Cu–Mg–Si system (Table 3.13), we have all necessary information for the calculation spreadsheet forms for all five-phase regions. The calculation of mass fractions is based on the following system of five linear equations:

\[
\begin{align*}
Q_{M1}C_{Si1} + Q_{M2}C_{Si2} + Q_{M3}C_{Si3} + Q_{M4}C_{Si4} + Q_{M5}C_{Si5} &= C_{SiX} \\
Q_{M1}C_{Cu1} + Q_{M2}C_{Cu2} + Q_{M3}C_{Cu3} + Q_{M4}C_{Cu4} + Q_{M5}C_{Cu5} &= C_{CuX} \\
Q_{M1}C_{Mg1} + Q_{M2}C_{Mg2} + Q_{M3}C_{Mg3} + Q_{M4}C_{Mg4} + Q_{M5}C_{Mg5} &= C_{MgX} \\
Q_{M1}C_{Fe1} + Q_{M2}C_{Fe2} + Q_{M3}C_{Fe3} + Q_{M4}C_{Fe4} + Q_{M5}C_{Fe5} &= C_{FeX} \\
Q_{M1}C_{A11} + Q_{M2}C_{A12} + Q_{M3}C_{A13} + Q_{M4}C_{A14} + Q_{M5}C_{A15} &= C_{A1X},
\end{align*}
\]
where $Q_{M1}, Q_{M2}, Q_{M3}, Q_{M4}, Q_{M5}$ are the mass fractions of the respective phases, and $C_{Si}, C_{Cu}, C_{Mg}, C_{Fe}, C_{Al}, C_{Si,X}$ etc. are the mass concentrations of Si, Cu, Mg, Fe, and Al in the $i$-phase and the analyzed alloy ($X$), respectively.

Figure A4.3 shows the spreadsheet for the calculation of Al–Si–Cu–Mg–Fe phase diagram. The user enters element concentrations for the analyzed alloy in the corresponding fields of the spreadsheet, and receives as a result the selection of phases with their mass and volume fractions. This spreadsheet can also be programmed for the calculation of (Al) composition at different temperatures. Figure 3.8a exhibits three possible sets of phases in the range of Al–Si alloys.

The properties of an alloy are to a great extent determined by the selection of phases and their amount. The suggested calculations can help in assessment of the effect of any given element on the values of $Q_M$ and $Q_V$ of all phases. An example of such a calculation is demonstrated in Figure 3.19 for the effect of silicon on the amount of excess phases in a 222.1 casting alloy. One can see a profound influence of this element.

The polythermal section of the Al–Cu–Fe–Mg–Si phase diagram at 10% Si, 5% Cu, and 0.5% Mg shown Figure 3.15 was constructed as follows. First, the position of liquidus lines and the polytherm of the beginning of the binary eutectic reaction $L \rightarrow (Al) + (Si)$ are assessed. Then the calculation shows that this section contains two invariant horizontals (Table 3.19), for the eutectic reaction $L \rightarrow (Al) + (Si) + Al_2Cu + Al_2Cu_2Mg_8Si_6 + Al_8FeMg_3Si_6$ at $\sim 505^\circ C$ and for the peritectic reaction

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
<th>F6</th>
<th>F7</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK5M7</td>
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<td>0.08</td>
<td>99.5</td>
<td>0</td>
<td>36.8</td>
<td>13.5</td>
<td>32.1</td>
</tr>
<tr>
<td>F1</td>
<td>1.8</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>19.2</td>
</tr>
<tr>
<td>F2</td>
<td>0.5</td>
<td>0.05</td>
<td>0</td>
<td>63.2</td>
<td>0</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>F3</td>
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<td>1</td>
</tr>
<tr>
<td>F5</td>
<td>87.7</td>
<td>90.82</td>
<td>0.5</td>
<td>47.5</td>
<td>0</td>
<td>59</td>
<td>15.7</td>
</tr>
<tr>
<td>Phase density</td>
<td>g/cm$^3$</td>
<td>(Al)</td>
<td>$Q_{M1} = 83.47$</td>
<td>$Q_{V1} = 84.79$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>2.7</td>
<td>(Si)</td>
<td>$Q_{M2} = 7.58$</td>
<td>$Q_{V2} = 8.00$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>R2</td>
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<td>$Al_2Cu$</td>
<td>$Q_{M3} = 3.349$</td>
<td>$Q_{V3} = 2.11$</td>
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<td></td>
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</tr>
<tr>
<td>R3</td>
<td>4.35</td>
<td>$Al_3FeSi$</td>
<td>$Q_{M5} = 2.35$</td>
<td>$Q_{V5} = 1.93$</td>
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</tr>
<tr>
<td>R4</td>
<td>1.88</td>
<td>$\pi$</td>
<td>$Q_{M7} = 3.25$</td>
<td>$Q_{V7} = 3.16$</td>
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<td></td>
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</tr>
<tr>
<td>R5</td>
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<tr>
<td>R7</td>
<td>2.82</td>
<td></td>
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</tr>
</tbody>
</table>

Figure A4.3. Excel spreadsheet for calculation of mass ($Q_M$) and volume ($Q_V$) fractions of phases in the Al–Cu–Fe–Mg–Si system in the range of Al–Si alloys.
\[ L + Al_5FeSi \Rightarrow (Al) + (Si) + Al_2Cu + Al_8FeMg_3Si_6 \] at \( \sim 554^\circ C \). And finally, the calculation of five-phase regions determines their boundaries.

It should be noted that the sections constructed using the described technique are quite similar to those produced with a thermodynamical software, provided the same starting data are used. Some of the sections of quaternary diagrams given in this book, e.g. Al–Cu–Mg–Si and Al–Fe–Ni–Si, were obtained by the authors using Thermocalc.