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Calculation and application of liquidus projection

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Abstract: Liquidus projection usually refers to a two-dimensional projection of ternary liquidus univariant lines at constant pressure. The algorithms used in Pandat for the calculation of liquidus projection with isothermal lines and invariant reaction equations in a ternary system are presented. These algorithms have been extended to multicomponent liquidus projections and have also been implemented in Pandat. Some examples on ternary and quaternary liquidus projections are presented.

Key words: liquidus projection; phase diagram; phase equilibrium; multicomponent system

1. Introduction

Liquidus projection is one of the important types of phase diagrams. Ternary liquidus projection at constant pressure onto a compositional plane is the most commonly used type. It shows the phase relationships between the liquid phase and the other phases. With the isothermal contour lines on the liquidus projection, a ternary liquidus projection gives a direct visualization of the liquidus surface. Rhines [1] presented in detail many ternary liquidus projections.

It is possible to calculate the liquidus projections for systems with more than three components. In this article, a method has been provided for calculating an *n*-component liquidus projection at constant pressure. An *n*-component liquidus projection consists of univariant liquidus lines. Information on these liquidus univariant lines can be stored in a multiple column table. Even though it is impossible to fully visualize a multicomponent liquidus projection in a space with more than three dimensions, it can be projected onto two- or three-dimensional space, which helps us understand the multicomponent liquidus surface.

In this article, Pandat, a multicomponent thermodynamic and phase diagram calculation software [2-4] is used to calculate the liquidus projections of the ternary and higher order systems. The ternary liquidus projections have been analyzed in detail. A few examples are presented for systems with special features such as liquid miscibility. The application of quaternary liquidus projection in the development of Zr-based bulk-metallic-glass is mentioned.

2. Calculation of ternary liquidus projection

Ternary liquidus projection is the most commonly used liquidus projection. To facilitate reading a two-dimensional liquidus projection, ternary isothermal contour lines are drawn on the same two-dimensional projection diagram. Fig. 1 is a calculated liquidus projection for the Nb-Ti-Si system. In this figure, the solid lines represent the compositions of the liquid in equilibrium with the other two phases. At an intersection point of the three different univariant liquidus lines, the liquid phase is in equilibrium with the other three phases. An invariant reaction occurs at this intersection point. The arrows

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on the univariant lines in Fig. 1 point to the directions of decreasing temperatures. The gray lines with labeled temperatures in the figure are the isothermal contour lines, which are the compositions of the liquid phase in equilibrium with another phase, i.e., the primary phase of solidification. The primary phases are also labeled in Fig. 1.

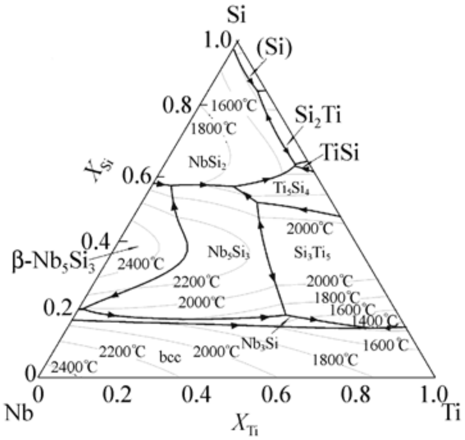

Fig. 1. Liquidus projection of the Nb-Ti-Si system with isothermal lines.

As long as all liquidus lines are connected, in principle, starting from any point on one of the liquidus univariant lines, it is possible to calculate all the liquidus univariant lines. If the univariant lines are disconnected, multiple starting points are required. As all the isothermal contour lines are disjointed, each isothermal line requires at least one starting point. All the starting points can be found by stepping through one or more one-dimensional scan lines in the composition space. The dashed lines in Fig. 2 show three such scan lines. For example, because scan line “a-b” passes through the liquidus univariant line $L \Leftrightarrow NbSi_2 + Nb_5Si_3$ at point “s”, the point “s” could be used as a starting point to calculate all liquidus univariant lines. The same method can be applied for the calculation of isothermal lines.

3. Calculation of the multicomponent liquidus projection

The ternary liquidus surface at fixed pressure is a surface in a three-dimensional space. It can be visualized in a three-dimensional space or projected onto two-dimensional planes. An *n*-component liquidus surface at fixed pressure is a hyper surface in an *n*-dimensional space of $(T, x_1, x_2, \cdots, x_{n-1})$. On this hyper surface, there exist equilibria from two-phase up to the (*n*+1)-phase.

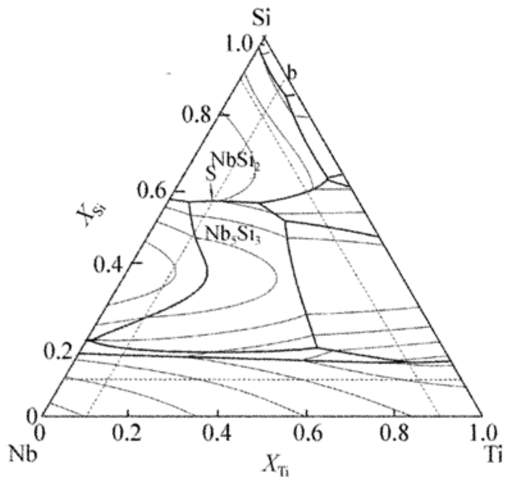

Fig. 2. Liquidus projection of the Nb-Ti-Si system. Scan lines (dashed lines) to the starting points for the univariant lines and the isothermal lines.

The most important types of phase equilibria are the *n*-phase univariant equilibrium and the (*n*+1)-phase invariant phase equilibrium, both involving at least one liquid phase. An (*n*+1)-phase invariant phase equilibrium locates at the intersection of the *n* *n*-phase univariant lines. The calculation of liquidus projection in an *n*-component system includes the calculation of the univariant equilibria between the liquid phase and the other *n*-1 phases and the intersection point of the univariant lines. The *n*-1 phases may also include the liquid phase if the latter forms miscibility gaps. The strategy to calculate the multicomponent univariant phase equilibria on the liquidus surface is the same as that for a ternary system presented in the previous section. At first, the starting points on some univariant lines are determined. The scan lines in the composition space will help locate such points. Next, the starting points are followed to calculate the liquidus univariant lines. When an invariant equilibrium point is found, a recursive algorithm leads to calculate the other *n*-1 liquidus univariant lines connected to the invariant intersection point. In contrast to the ternary systems, multicomponent isothermal contours are not univariant anymore. The calculation of the multicomponent isothermal contour lines requires extra compositional constraints. An example of the quaternary liquidus projection Cu-Ni-Ti-Zr will be presented later.

4. Importance of stable phase equilibrium

Similar to the other types of phase-diagram calculations, the major difficulty encountered in the liquidus projection calculation lies in determining the stable phase equilibria. The software used here for the liquidus projection calculation is Pandat [2-4], in which a global minimization algorithm is implemented. After each phase equilibrium is calculated on the univariant line or the isothermal contour line, its stability is examined against all the phases considered in the system, including the liquid phase, which ensures that the calculated phase equilibria on the liquidus surface are always stable. This can be appreciated especially when a phase, liquid or another phase, exhibits a miscibility gap. It is difficult for a user to guess where the miscibility gaps will occur. Only a global minimization algorithm can avoid the users' input for the initial values for the calculation of liquidus projection and make the calculation automatic.

5. Invariant reactions

Rhines summarized the reaction types in his classic book "*Phase Diagrams in Metallurgy*" [1]. A reaction type such as "class I" is a useful terminology in ternary or quaternary systems. Some of the reaction types are still used in higher order systems such as the eutectic reaction (class I). However, it is cumbersome to use this notation in many other cases. For a multicomponent liquidus projection, an invariant reaction equation is more suitable for representing the invariant equilibrium information. A simple algorithm to determine the invariant reaction type is presented here.

A binary system is used as an example to illustrate the method for determining an invariant reaction equation. Fig. 3 shows schematic diagrams for two types of invariant reactions. Let T* be the invariant temperature. It is apparent that Fig. 3(a) has an invariant reaction of $L \Leftrightarrow \alpha+\beta$, whereas Fig. 3(b) has an invariant reaction of $L+\alpha \Leftrightarrow \beta$. The following algorithm can be used to determine the reaction equations.

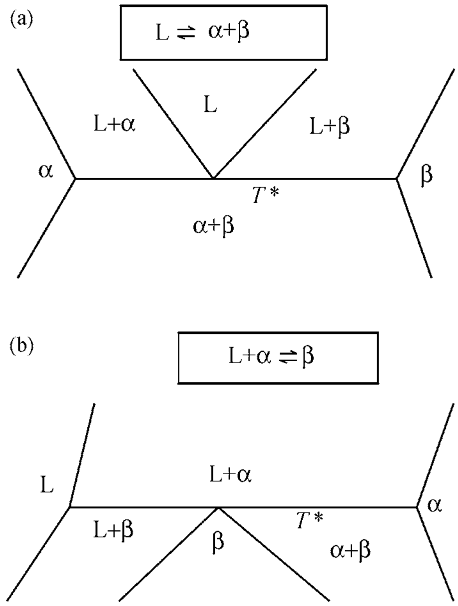

Fig. 3. Schematic diagrams for two types of invariant reactions.

First, the three-phase equilibrium $L+\alpha+\beta$ must be verified as a stable invariant equilibrium using the global minimization algorithm mentioned in the previous section. Next, the two-phase equilibria from all combinations of the three phases are calculated at a temperature slightly above the invariant temperature, $T^*+\delta T$. A set of *stable* two-phase equilibria will be obtained for this temperature. If a phase belongs to every one of the stable two-phase equilibria at the temperature of $T^*+\delta T$, this phase is a reactant. Otherwise, it is a product. In the reaction equation, a phase is either a reactant or a product. If a phase, liquid or solid, has a miscibility gap, this phase will appear more than once in the set of phases of the invariant reaction.

In the case of the reaction in Fig. 3(a), $L+\alpha$ and $L+\beta$ are the stable two-phase equilibria at $T^*+\delta T$. Only the liquid phase belongs to both stable two-phase equilibria at the given temperature. Therefore, the liquid phase is the only reactant, and the phases α and β are the products. The reaction equation can be written as $L \Leftrightarrow \alpha+\beta$. For the invariant reaction in Fig. 3(b), it can be seen that only one two-phase equilibrium, $L+\alpha$, is stable at $T^*+\delta T$. Since both liquid and α belong to this sole stable two-phase equilibrium, these two phases are the reactants, and the other phase, β, is the only product. The reaction equation is then $L+\alpha \Leftrightarrow \beta$ for the invariant reaction in Fig. 3(b).

The algorithm presented here can be used for determining the multicomponent invariant reactions, which has been implemented in Pandat [2-4].

6. Examples

In this section, two examples are presented to illustrate the special features in ternary liquidus projections, one with constant-temperature univariant liquidus lines; and the other with a liquidus miscibility gap. The third example is a demonstration of the Cu-Ni-Ti-Zr quaternary liquidus projection, which has been used in the development of Zr-based bulk metallic glass.

6.1. Ternary Ni-Al-Cr system with constant-temperature univariant lines

Fig. 4 shows the liquidus projection for the ternary system Ni-Al-Cr [5], which shows an interesting feature. Usually, temperature in a liquidus univariant line changes with the composition. However, the univariant lines for $L+Al_9Cr_4\_L+Al_9Cr_4\_H$ and $L+Al_8Cr_5\_L+Al_8Cr_5\_H$ are the constant-temperature lines with a temperature of 1060°C and 1125°C, respectively. These two lines are plotted as gray lines for distinguishing from the other univariant lines. The reason for the constant-temperature univariant lines is that the binary phases are modeled as stoichiometric phases with the same composition.

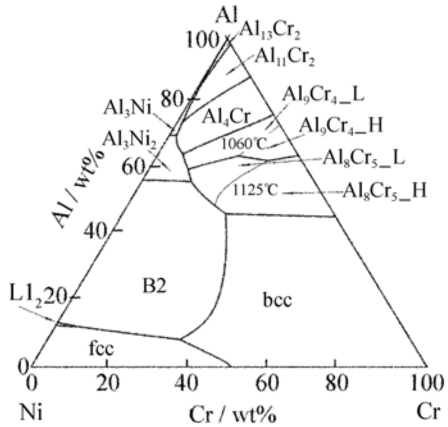

Fig. 4. Calculated liquidus projection of the Ni-Al-Cr system [5].

6.2. Ternary system Al-Mg-Sc with liquid miscibility gap

In the ternary Al-Mg-Sc system [6], even though there is no liquid miscibility gap in the three constituent binary systems, the liquid phase forms a miscibility gap in the central part of the ternary system as shown in Fig. 5. It is not unusual that the liquid phase forms a miscibility gap in multicomponent systems. An automatic search for the most stable phase equilibria in Pandat enables the automatic calculation of liquidus projection even with miscibility gaps.

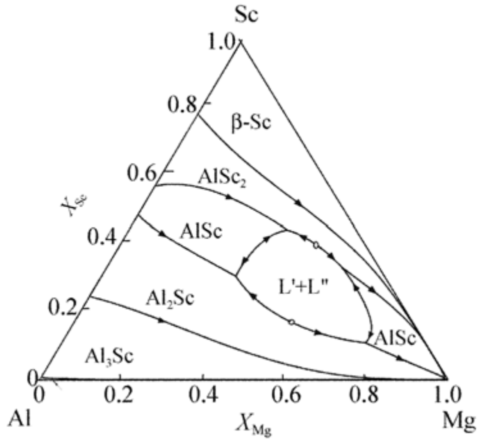

Fig. 5. Liquidus projection of Al-Mg-Sc [6]. The open circles represent the maximum temperatures on the univariant lines.

6.3. Quaternary system Zr-Cu-Ni-Ti

Zr-Cu-Ni-Ti is the base system for forming Zr-based bulk-metallic-glass. It is found that the bulk-metallic-glass forming regions are closely related to the regions with the lowest melting temperatures [7]. Calculation of the liquidus projection will provide the information on the composition regions with the lowest melting temperatures.

Fig. 6 shows the liquidus projection on the planes of the temperature and the individual composition of the components. Overlapping of the univariant lines are found in this figure. It is possible, but very difficult, to read the invariant temperatures and the corresponding compositions of the components from Fig. 6. Accurate information on the invariant reactions is listed in the Pandat interface after the calculation. The invariant reaction equation for the eutectic with the lowest temperature is found to be $L \Leftrightarrow CuZr_2 + NiTiZr + bcc + Cu_2TiZr$ with a eutectic temperature of 695.3°C and the composition of the liquid phase: $x_{Cu} = 0.1475$, $x_{Ni} = 0.1416$, $x_{Ti} = 0.2715$, and $x_{Zr} = 0.4394$.

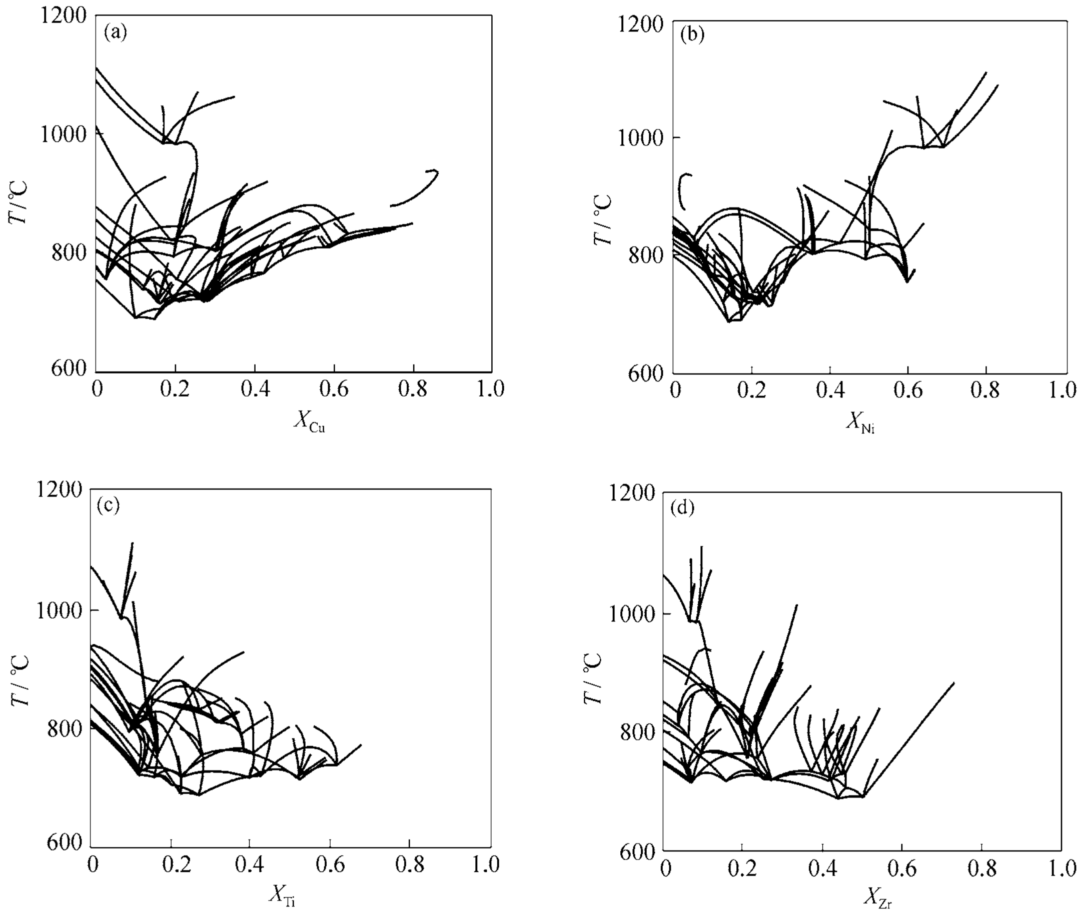

Fig. 6. Liquidus projection for Cu-Ni-Ti-Zr on the temperature vs. mole fraction planes.

Fig. 7 is a projection diagram, which shows only the compositions of invariant reactions with the lowest temperatures. The regions with the lowest temperatures tend to form the bulk-metallic-glasses. A comparison with the experimental data [8], also shown in this diagram, confirms that the compositions in the calculated low-lying invariant reaction regions have an increasing tendency to form bulk-metallic-glasses.

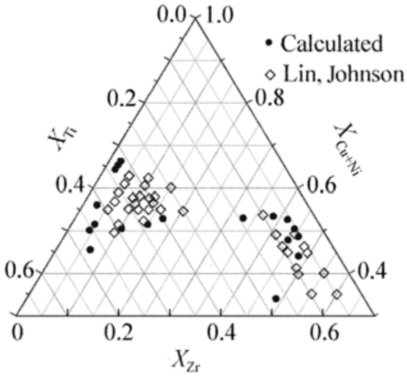

Fig. 7. Comparison of the thermodynamically predicted and experimentally identified [8] liquid compositions of the five-phase invariant reactions with one of the phases being liquid in the Zr-Cu-Ni-Ti system.

7. Summary

A novel method was presented to calculate liquidus projections, the univariant equilibrium lines involving the liquid phase, for ternary and multicomponent systems. The isothermal lines were also calculated in the ternary systems. A simple algorithm was proposed for the determination of the invariant reaction equations. For an (n+1)-phase invariant reaction, if a phase is involved in every one of the stable n-phase equilibria at a temperature just above the invariant temperature, the phase is a reactant; otherwise, the phase is a product.

The importance of the stability of the calculated phase equilibria has been emphasized. Only a global minimization algorithm can ensure that the calculated liquidus univariant and the invariant phase equilibria are stable. A multidimensional global minimization algorithm has been implemented in Pandat, which was used for calculating the liquidus projections in the present study.

Three examples of the liquidus projections were provided. Two of these illustrate the special features in the ternary liquidus projections, one with constant-temperature univariant lines and the other with a liquidus miscibility gap. The third example is the Cu-Ni-Ti-Zr quaternary liquidus projection, which has been used in the development of Zr-based bulk-metallic-glass.

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