Plotting phase diagrams of binary alloys and justification of their industrial use

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Abstract. Binary eutectic solutions are analyzed as a foundation for a Generalized Lattice Model of each component. Phase transitions of binary solutions depending on concentration of its components and temperature are determined with equations for invariant two-phase equilibriums by construction of binary-phase diagrams. The paper demonstrates a possibility to construct binary-phase diagrams with minimal error with respect to reference sources. An example of cadmium-zinc alloy is used to show changes in its characteristics depending on percentages of its components. An application is suggested for items with cadmium-zinc coating.

1. Introduction
Alloys are industrial or commercial materials which are a mixture of several chemical elements. Liquid alloys are un-oriented materials. Properties of un-oriented materials pose more difficulties for understanding than their properties in the solid state. Some idea of influence from liquid solutions may be obtained from studying solid materials. It is facilitated by eutectic state diagrams. Such diagrams may be constructed either from theoretical equations or from experimental data. Both methods have their advantages and disadvantages in obtaining reliable results, at that, of course, the optimal path is a combination of both. Theoretically constructed dependencies are further confirmed with experimental studies, or experimental data are used to correct the theoretical equations.

Eutectic systems always kindled a significant interest of both experimenters and theoreticians [1]. Eutectic diagram contains eutectic curves reflecting two-phase state of a two-phase alloy, where each point reflects the values of the alloy’s physical parameters that characterize its state.

Thanks to eutectoid diagrams, a picture of phase transitions may be obtained for cooling (heating) of binary alloys with various percentages of their components.

One of the urgent tasks is modeling the calculation methods for construction of phase diagrams of eutectic solutions from the properties of a generalized lattice model (GLM) of solution.

2. Theoretical calculations
According to the basic principles of GLM and known theromodynamic equilibrium equations [2], chemical potentials $\mu_1$ and $\mu_2$ of a uniform binary solutions of components 1 and 2 (taken as per 1 mole of substance) may be represented as:
\[ \mu_1 = \mu_{i0} + RT \ln x + W \lambda \left( \frac{1-x}{x+\lambda(1-x)} \right)^2 \]

\[ \mu_2 = \mu_{20} + RT \ln(1-x) + W \left( \frac{x}{x+\lambda(1-x)} \right)^2 \]

where \( \mu_{i0} \) is a standard value of chemical potential for the \( i \)-th component, \( R \) is the universal gas constant, \( T \) is the system temperature, \( x \) is the molar fraction of the first component, \( W \) is a counterpart for mixing energy in the Generalized Lattice Model, \( \lambda = \omega_2/\omega_1 \), where \( \omega_i \) is the size (radius) of the \( i \)-th component atoms, introduced with the conditions of close packing of atoms.

Let us analyze the eutectic phase diagram with partial solubility of components in the solid state (Figure 1). Let \( x, y \) and \( z \) be molar fractions in liquid phase, in solid alpha-solution and solid beta-solution, respectively. We are going to denominate the counterpart for mixing energy of molten metal and solid \( \alpha \)- and \( \beta \)-solutions with the letters \( W, U, G \).

**Figure 1.** Eutectic phase diagram when there is a mutual solubility of components in solid state

The system of equations (1) determines concentration dependency of chemical potential values of the components in the liquid alloy phase. Let us construct similar equations for solid \( \alpha \)- and \( \beta \)-solutions:

– for \( \alpha \)-solution

\[ \mu_1^\alpha = \mu_{10} + RT \ln y + U \lambda \left( \frac{1-y}{y+\lambda(1-y)} \right)^2 \]

\[ \mu_2^\alpha = \mu_{20} + RT \ln(1-y) + U \left( \frac{y}{y+\lambda(1-y)} \right)^2 \]

– for \( \beta \)-solution

\[ \mu_1^\beta = \mu_{10} + RT \ln z + G \lambda \left( \frac{1-z}{z+\lambda(1-z)} \right)^2 \]

\[ \mu_2^\beta = \mu_{20} + RT \ln(1-z) + G \left( \frac{z}{z+\lambda(1-z)} \right)^2 \]

For subsequent calculations, it is necessary to determine for parameters of GLM: \( W, U, G \) and \( \lambda \). With that in mind, let us consider invariant three-phase equilibrium, characterized with composition of corresponding phases \( x, y, z \) at an eutectic temperature \( T_0 \). From the general condition of phase equilibrium (a state, where the phases of a thermodynamic system are in thermal, mechanical and chemical equilibrium) for eutectic transition, we have the following, according to [3, 4]

\[ \mu_i^L(x_i, T_0) = \mu_i^\alpha(y_i, T_0) = \mu_i^\beta(z_i, T_0) \]

\[ \mu_i^L(x_i, T_0) = \mu_i^\alpha(y_i, T_0) = \mu_i^\beta(z_i, T_0) \]

\[ \mu_i^L(x_i, T_0) = \mu_i^\alpha(y_i, T_0) = \mu_i^\beta(z_i, T_0) \]
Subsequent calculations of the phase diagram are based on studying two-phase equilibriums above (or below) the eutectic temperature. Having equated relevant chemical potentials and following [3, 4], let us find out concentration dependencies for boundaries of two-phase areas in the phase diagram being analyzed:

1) Liquid – solid α-solution equilibrium ($x > x_0$, $y > y_0$, $T > T_0$):

$$T(x, y) = \frac{q_1 T_1 + W\lambda(-\frac{1-x}{x+\lambda(1-x)})^2 - U\lambda(-\frac{1-y}{y+\lambda(1-y)})^2}{q_1 - \ln(x/y)}$$

$$q_2 T_2 + W\left(-\frac{x}{x+\lambda(1-x)}\right)^2 - U\left(-\frac{y}{y+\lambda(1-y)}\right)^2 = \frac{q_2 - \ln(1-x/1-y)}{}$$

(5)

2) Liquid – solid β-solution equilibrium ($x < x_0$, $z < z_0$, $T > T_0$):

$$T(x, z) = \frac{q_1 T_1 + W\lambda(-\frac{1-x}{x+\lambda(1-x)})^2 - G\lambda(-\frac{1-z}{z+\lambda(1-z)})^2}{q_1 - \ln(x/z)}$$

$$q_2 T_2 + W\left(-\frac{x}{x+\lambda(1-x)}\right)^2 - G\left(-\frac{z}{z+\lambda(1-z)}\right)^2 = \frac{q_2 - \ln(1-x/1-z)}{}$$

(6)

3) Solid α-solution – solid β-solution equilibrium ($y < y_0$, $z < z_0$, $T < T_0$):

$$T(y, z) = \frac{G\lambda(-\frac{1-z}{z+\lambda(1-z)})^2 - U\lambda(-\frac{1-y}{y+\lambda(1-y)})^2}{q_1 - \ln(z/y)}$$

$$G\left(-\frac{z}{z+\lambda(1-z)}\right)^2 - U\left(-\frac{y}{y+\lambda(1-y)}\right)^2 = \frac{q_2 - \ln(1-y/1-z)}{}$$

(7)

In order to calculate the $q_i$ values, it is necessary to determine a difference between standard values of chemical potentials of the components in solid and liquid phases. This task is solved with traditional methods of statistical thermodynamics without using a specific model of the solution. So, according to [5]:

$$q_i = H_i/RT_i,$$

(8)

where $H_i$ are the latent heat values for liquid-solid transition in unalloyed components; $T$ is the melting temperature of unalloyed components.

Equations for chemical potentials (1)-(3) and equilibrium conditions (4) form a closed system of equations, whose solutions allow finding all the GLM parameters: $W = W/R$, $U = U/R$, $G = G/R$, $\lambda$ for specific eutectic systems of A-B solutions. (Table 1).

Solving equations (5)-(7) allows constructing a closed system of equation and finding...
concentration dependencies of liquidus branch (for phase diagrams, it is a line of complete melting of solid phases), solidus branch (a line in phase diagrams where the last drops of liquid melted material disappear) and solvus (points with such a temperature that solid phases with variable chemical compositions coexist with other solid phases) within the GLM framework and plotting phase diagrams for binary solutions with partial solubility of components in the solid state.

Table 1. GLM parameters of binary systems.

| A-B     | q₁   | q₂   | λ    | W̃, K | Ũ, K | G̃, K |
|---------|------|------|------|-------|-------|-------|
| Ag-Cu  | 1.152| 1.097| 1.126| 1623  | 3427  | 2983  |
| Al-Ge  | 2.959| 1.379| 0.901| -1248 | 3171  | 2368  |
| Bi-Cd  | 1.296| 2.407| 0.747| 69    | 1557  | 1312  |
| Cd-Zn  | 1.264| 1.296| 0.932| 2376  | 2376  | 1673  |

3. Analysis of theoretical calculations and comparison against experimental data

This model was used in calculations for several eutectic phase diagrams of alloys with solubility of components in the solid state (Ag-Cu, Al-Ge, Bi-Cd, Cd-Zn). The table shows GPM values for the binary systems that correspond to the type being analyzed. Reference values for latent heat of liquid-solid transition were used for qi calculations [6]. Solution of the system produced the following phase diagrams (Figures 2, 3).

It is evident that the final values of the equilibrium state curve for the selected solutions correspond to reference data [7] with error values not exceeding 2-3%.

Figure 2. Phase equilibrium diagram: a – Ag-Cu; b – Al-Ge (points represent reference data from [6], continuous curves are calculated).
Figure 3. Phase equilibrium diagram: a – Bi-Cd; b – Cd-Zn (points represent reference data from [7], continuous curves are calculated).

4. Application of binary alloys in the oil industry

Today, the oil industry faces a lot of challenges. One of them is a search for an alloy that is highly corrosion resistant for prolonged operation in aggressive media and has high strength characteristics allowing increased loading, with a relatively low cost [8-10].

The need for such alloys is due to the following factors: construction of deep wells with complex profiles, resulting in operation of equipment at increased pressure and load values; advanced production methods requiring application of chemically active substances and thermal recovery methods, etc. [11-13].

Let us consider the latter of the alloys considered in the theoretical part, namely Cd-Zn, with electric potentials of pure metals equal to negative 0.403 and negative 0.763, respectively. Even while the difference in potential is low, zinc and cadmium provide relatively good protection against contact corrosion.

Zinc coatings are well-known for their corrosion resistance and are used for pipeline protection. Zinc is an inexpensive and readily-available metal. It provides both mechanical and electrochemical protection of coated items thanks to a protective film formed when zinc metal is oxidized on contact with the environment.

Zinc coatings are common around the globe. More than 20% of steel parts are protected against corrosion with zinc. It is also known, that about 50% of all zinc produced are used in galvanizing.

Let us now consider cadmium. It has a value of potential closer to that of iron (electric potential of negative 0.44) than zinc. The degree of cadmium protection is determined by corrosive medium. For instance, in humid atmosphere, cadmium’s potential becomes more electro-negative than that of iron. It provides electrochemical protection against corrosion. Some characteristics of Zn and Cd metals are shown in Table 2.

Table 2. Characteristics of metallic Zn and Cd.

| Name               | Zn  | Cd  |
|--------------------|-----|-----|
| Melting point, °C  | 419 | 321 |
| Tensile strength, MPa | 150 | 75  |
| Shear strength, MPa | 68.5| 31.43|

So, why use a cadmium-zinc alloy? This alloy has a number of advantages over its components taken separately. The advantages result
from increased strength, this alloy may be used for manufacture of small items, because it has a good castability. Most significantly, the corrosion resistance of the alloy exceeds that of its components. The only drawback of the cadmium-zinc alloys are relatively low melting point values [14].

Small content of cadmium reduces the melting point of cadmium-zinc alloys, improves thermal and electrical conductivity and improves mechanical properties, such as hardness, wear resistance, tensile strength and fatigue endurance [15], thus, application of zinc in a combination with cadmium is preferable.

A Cd-Zn alloy may have different properties at differing component concentrations (Table 3). In the US, cadmium-zinc alloy has already found a wide field of application. For instance, American Elements supplies cadmium-zinc alloy-based coatings with various combination of the components for the needs of oil industry. For example, they supply pipes covered in Cd-Zn to protect them against corrosion and powder mix for subsequent coating of unprotected pipes [16].

Table 3. Properties of various Cd-Zn alloys.

| Composition (%) | 83Cd - 17Zn | 70Cd - 30Zn | 60Cd - 40Zn |
|-----------------|-------------|-------------|-------------|
| Melting point, °C | 346         | 320         | 305         |
| Tensile strength, MPa | 165.7       | 186.6       | 206.8       |
| Shear strength, MPa | 75.8        | 82.7        | 89.6        |

5. Conclusion

Plotting binary phase diagrams may be useful for studying known alloys with varying concentrations and for development of new alloys with varying compositions of metals. For example, the Cd-Zn alloy has different melting points and mechanical properties for different concentrations. It may be used for metal coating where additional strength of the protective film is needed and equipment is operated at relatively low temperatures (100-150 °C), under increased humidity, in salt-loaded environments, for example in operating conditions typical of items used in the oil industry in marine and tropical climate.

References
[1] Thomson C V and Spaepen F 1979 On the approximation of the free energy change on crystallization Acta. Met. 27 1855
[2] Elliott R 1962 Factors affecting the solute distribution during the normal freezing of lead-antimony alloys J. Inst. Metals 90 447
[3] Bhatia A B and Thornton D E 1970 Structural aspects of the electrical resistivity of binary alloys Phys. Rev. B 2(8) 3004–3012
[4] Akinlade O, Singh R N and Sommer F 1998 Thermodynamic investigation of viscosity in Cu–Bi and Bi-Zn liquid alloys J. Alloy. Compd. 267 195–198
[5] Singh R N and Sommer F 1998 Thermodynamic investigation of viscosity and diffusion in binary liquid alloys Phys. Chem. Liq. 36 17-28
[6] Chung S, Jung W and Pak J 2002 Activity measurement of Zn in liquid Zn–Cd alloy using EMF method Korean J. Mater. Res. 12(4) 283–289
[7] Katayama I, Maki K, Fukuda Y, Ebara A and Iida T 1997 Thermo-dynamic activity of liquid Zn–Cd alloys studied by EMF method with zirconia solid electrolyte Mater. T. Jim. 38(2) 119–122
[8] Galiullina I F and Kadyrov R R 2018 Technical and economic background for siting production of well-killing liquid at oil fields IOP Conference Series: Earth and Environmental Science 194(8) 082013
[9] Shacurov N G 2019 Formation of a system for predicting the reliability of structural materials Atlantis Highlights in Material Sciences and Technology (AHMST): Int. Symp. "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019) vol 1 DOI:
10.2991/isees-19.2019.163.

[10] Nurgaliev R Z, Kozikhin R A, Fattakhov I G, Kuleshova L S and Gabbasov A Kh 2019 Prospects for the use of new technologies in assessing the impact of geological and technological risks *IOP Conference Series: Earth and Environmental Science (Int. Conf. on Innovations and Prospects of Development of Mining Machinery and Electrical Engineering 2019, IPDME 2019)* **378**(1) 012117 DOI: 10.1088/1755-1315/378/1/012117.

[11] Filimonov O V and Galiullina I F 2018 Area of reservoir heating during steam cyclic treatment of oil wells *IOP Conference Series: Earth and Environmental Science* **194**(8) 082010

[12] Rakhimov N R, Umarova G A and Zakirova Kh D 2019 Studying optoelectronic detectors for fatigue parameters control on machine-building metal surfaces *Journal of Physics: Conference Series* **1333**(6) 062022 DOI: 10.1088/1742-6596/1333/6/062022.

[13] Gilmanova A M 2019 Metrological support of geophysical equipment for acoustic logging *IOP Conference Series: Earth and Environmental Science (Int. Conf. on Innovations and Prospects of Development of Mining Machinery and Electrical Engineering 2019, IPDME 2019)* **378**(1) 012080 DOI: 10.1088/1755-1315/378/1/012080.

[14] Koirala R P, Singh B, Jha I and Adhikari D 2013 Thermodynamic, structural and surface properties of liquid Cd–Zn alloys *Journal of Molecular Liquids* **179** 60-66

[15] Awe O E and Azeez A A 2017 Temperature dependence of the bulk and surface properties of liquid Zn–Cd alloys *Applied Physics A*. **123** (Springer-Verlag Berlin Heidelberg)

[16] Zanvettor C M A and Marques J M C 2014 On the lowest-energy structure of binary Zn–Cd nanoparticles: Size and composition *Chemical Physics Letters* **608** 373-379