

CALCULATION OF TEMPERATURE DEPENDENCES OF THERMAL EFFECTS AT COOLING OF METAL ALLOYS

РАСЧЕТ ТЕМПЕРАТУРНЫХ ЗАВИСИМОСТЕЙ ТЕПЛОВЫХ ЭФФЕКТОВ ПРИ ОХЛАЖДЕНИИ МЕТАЛЛИЧЕСКИХ СПЛАВОВ

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Abstract: A method is proposed for determining the temperature dependences of thermal effects (the amount of heat released when the temperature changes) based on data on the temperature-concentration dependences of the free energies of the phases of metallic systems. These dependences are necessary for modeling of the processes of crystallization of alloys. They make it possible to obtain temperature dependences of the dimensions of the thermal effects without introducing the results of measurements of direct calorimetry. The peculiarity of calculating of the temperature dependences of thermal effects upon cooling of binary metal systems from the liquid state to room temperature (including crystallization) is shown using the example of the alloy of the system Pb-Sn.

KEYWORDS: ENTHALPY, HEAT CAPACITY, CRYSTALLIZATION, PHASE DIAGRAM

1. Introduction

Mathematical modeling of crystallization and formation of the structure of metal castings [1], including of castings with freezing [2], is of considerable practical interest. The degree of reliability of such models is largely determined by the accuracy of the temperature dependences of the thermal effects associated with the cooling of the metal. The problem of the availability of such dependencies is particularly acute when it comes to crystallization of alloys, as transformations in multi-component systems occur mostly in the temperature range where the system is in a heterophase state. And for most alloys, only data of the heat capacity averaged over the temperature and composition are generally available.

2. Solution of the problem under consideration

At the same time, data on the temperature-concentration dependences of the free Gibbs energies of the phases forming the system under consideration for many metallic systems are given in the literature. For example, for the case of a two-component system, the molar free energy and enthalpy of the phase are determined as [3]:

$$G(x, T) = G_A(T) \cdot (1 - x_B) + G_B(T) \cdot x_B + G_{mix}(x, T) + RT \cdot (x_A \ln x_A + x_B \ln x_B), \quad (1)$$

$$H(x, T) = H_A(T) \cdot x_A + H_B(T) \cdot x_B + H_{mix}(x, T), \quad (2)$$

where $G_A(T)$, $G_B(T)$ – are the molar free energy of pure components A and B in the phase at a temperature T ; $x_A = (1 - x_B)$, x_B – contents of components A and B in the phase (molar fractions); $G_{mix}(x, T)$ is the excess molar free energy of mixing in the phase of composition x at temperature T ; $H_A(T)$, $H_B(T)$ – are molar enthalpies of pure components A and B in the phase at a temperature T ; $H_{mix}(x, T)$ is the molar enthalpy of mixing in the phase of the composition x at temperature T .

The temperature-concentration dependences of the excessive mixing energies in phases ($G_{mix}(x, T)$) are widely given in literary sources (they are used to calculate state diagrams). In addition, if the phase structure coincides with the structure of the pure component in the aggregate state under consideration, then its molar enthalpy in the phase ($H_A(T)$ or $H_B(T)$) can be determined from the data on the temperature dependence of the heat capacity ($H = \int C_p dT$). A certain complexity is the determination of the heat capacity of the components in phases whose structures differ from the structure of the component in pure form (for example, in

the Al-Si system, silicon, which in its pure form does not have a FCC lattice, is included in the FCC structure of the solid state solution based on aluminum). However, for most metal systems the data are widely represented in the literature (they are also used to calculate the state diagrams) on the lattices' stability parameters (on the temperature dependences of the differences of the molar free energies of pure components in the standard state (as a rule – in liquid one) and in the state with the structure under consideration (with a certain type of crystal lattice)). Therefore, the problem is reduced to the determination of enthalpy of mixing and enthalpies of pure components in phases with the help of known dependences of excess free energy of mixing and of stability parameters of components' lattices. The solution of this problem is complicated by the fact that in expressions for free energies, the entropic and enthalpy terms, as a rule, are not separated.

At the same time, the magnitudes of enthalpy, entropy and isobaric-isothermal potential are interconnected through the heat capacity C_p :

$$\left. \begin{aligned} H &= \int C_p dT, \\ S &= \int \frac{C_p}{T} dT, \\ G &= H - TS = \int C_p dT - T \int \frac{C_p}{T} dT. \end{aligned} \right\} \quad (3)$$

If the temperature-concentration dependence of the excess molar heat capacity of mixing ($C_p^{mix}(x, T)$) in the phase is expressed as a polynomial

$$C_p^{mix}(x, T) = m_3^{mix}(x) + m_4^{mix}(x)T + \frac{m_5^{mix}(x)}{T^2} + m_6^{mix}(x)T^2 + m_7^{mix}(x)T^3 + \dots, \quad (4)$$

then, in accordance with (3), expressions for molar enthalpies and excess free energy of mixing will take the form [4, 5]:

$$H_{mix}(x, T) = m_1^{mix}(x) + m_3^{mix}(x)T + \frac{m_4^{mix}(x)T^2}{2} - \frac{m_5^{mix}(x)}{T} + \frac{m_6^{mix}(x)T^3}{3} + \frac{m_7^{mix}(x)T^4}{4} + \dots, \quad (5)$$

$$G_{mix}(x, T) = m_1^{mix}(x) - m_2^{mix}(x)T + m_3^{mix}(x)T(1 - \ln T) - \frac{m_4^{mix}(x)T^2}{2} - \frac{m_5^{mix}(x)}{2T} - \frac{m_6^{mix}(x)T^3}{6} - \frac{m_7^{mix}(x)T^4}{12} + \dots \quad (6)$$

where $m_1(x)$ and $m_2(x)$ are the integration constants.

The dependence of the specific heat of mixing on the composition can be taken into account by introducing of each of the coefficients in (4) in the form of polynomials:

$$m_k^{mix}(x) = m_{k,1}^{mix}(x) + m_{k,2}^{mix}(x)x + m_{k,3}^{mix}(x)x^2 + \dots \quad (7)$$

In the same way, by introducing of changes of the components' heat capacity in the transition from the standard state to the state under consideration in the form of polynomials,

$$\Delta C_p^i(T) = m_3^i + m_4^i T + \frac{m_5^i}{T} + m_6^i T^2 + m_7^i T^3 + \dots, \quad (8)$$

it is possible to obtain expressions for the temperature dependences of changes of molar enthalpies and free energies of pure components during phase transitions:

$$\Delta H^i(T) = m_1^i + m_3^i T + \frac{m_4^i T^2}{2} - \frac{m_5^i}{T} + \frac{m_6^i T^3}{3} + \frac{m_7^i T^4}{4} + \dots \quad (9)$$

$$G^i(T) = m_1^i - m_2^i T + m_3^i T(1 - \ln T) - \frac{m_4^i T^2}{2} - \frac{m_5^i}{2T} - \frac{m_6^i T^3}{6} - \frac{m_7^i T^4}{12} + \dots \quad (10)$$

3. Results and discussion

The idea of the proposed method is based on the thesis that, in the presence of analytical expressions for the temperature-concentration dependence of the excess molar free energy of mixing in the phase and the temperature dependences of the stability parameters of the components' lattices, their values can be determined for an arbitrarily large number of values of temperatures and compositions from the phase's region of the existence. And the values of coefficients m^{mix} and m^i which are interesting for us can be determined by solving the system of equations obtained by equating expressions (6) and (10) with the calculated values of the free energy of the phase and of the stability parameters of the components' lattices. As a result, we obtain the temperature-concentration dependences of the enthalpy and the heat capacity of the mixing, as well as the temperature dependences of the changes of the components' enthalpies and heat capacities at phase transitions.

The enthalpy of a heterogeneous system is defined as the sum of enthalpies of individual phases. Therefore, the change of the enthalpy in the transition of a multiphase system from one state to another one is defined as the difference of sums of the phases' enthalpies in these states. In calculating changes of the heterogeneous system's enthalpy caused by changes of temperature, changes of the compositions and quantities of phases remaining in equilibrium (in accordance with the state diagram) must also be taken into account.

The peculiarities of the application of the proposed methodology were investigated on the example of modeling of cooling of the alloy of the system Pb-Sn, containing 36.35 wt. % Sn ($a = 0.499$ of mole fractions of Sn). Temperature dependencies of thermal effects were calculated at cooling in the range of a temperature from 290°C (563 K) to 30°C (303 K). The whole period of temperature's variation was split into intervals $\Delta T = 1$ K. Changes of enthalpy were determined for each of these intervals. The step of temperature's change $\Delta T = 1$ K provides the required accuracy of the calculation. In addition, the thermal effect accompanying cooling by 1K can formally be considered as the average heat capacity in the specified range of temperature. This allows us to apply algorithms of the simulation of crystallization of pure metals [2] to calculate the crystallization of multicomponent alloys. Thermal effects were determined on the basis of 1 mol of alloy. The temperature dependences of the heat capacity of pure components in the liquid state are taken from [6]. The enthalpies of mixing in phases (Table 1) were determined according to the abovementioned method, based on the data on the excess free mixing energies [7]. In

accordance with the thermodynamic phases adopted in [7], the values of the enthalpy of mixing in all phases of the Pb-Sn system depend only on the composition and do not depend on the temperature (the heat capacity of the mixing is zero).

Table 1. Dependences of Enthalpies of Mixing in the Phases of Pb-Sn System

Phase	Enthalpy of mixing $H_{mix}(x, T)$, J/Mole
Melt (L)	$x(1-x)(4800 + 200 \cdot x)$
FCC solid solution based on plumbum (Pb)	$x(1-x)(6700 - 0.365 \cdot x)$
BCC tin solid solution (Sn) OCT solid solution based on tin (Sn)	$x(1-x)(-203068)$

According to the state diagram of the system Pb-Sn [7], at temperatures above 234°C (507 K), the considered alloy is in a single-phase liquid state (Figure 1). Therefore, the thermal effects (changes of enthalpy) when cooling of 1 mol of alloy by $\Delta T_j = T_{j+1} - T_j$ in the indicated region of temperature are defined as:

$$Q_i = (1-x) \cdot \Delta H_i^{Pb} + x \cdot \Delta H_i^{Sn} + \Delta H_i^{mix}(x_i, T_i), \quad (11)$$

where $\Delta H_j^{Pb} = \int_{T_j}^{T_{j+1}} C_p^{Pb}(T) dT$, $\Delta H_j^{Sn} = \int_{T_j}^{T_{j+1}} C_p^{Sn}(T) dT$ - changes

of the molar enthalpies of pure tin and plumbum in the liquid phase when it is cooled by ΔT_j , $C_p^{Pb}(T)$ and $C_p^{Sn}(T)$ - the temperature dependences of the molar heat capacity of liquid plumbum and tin;

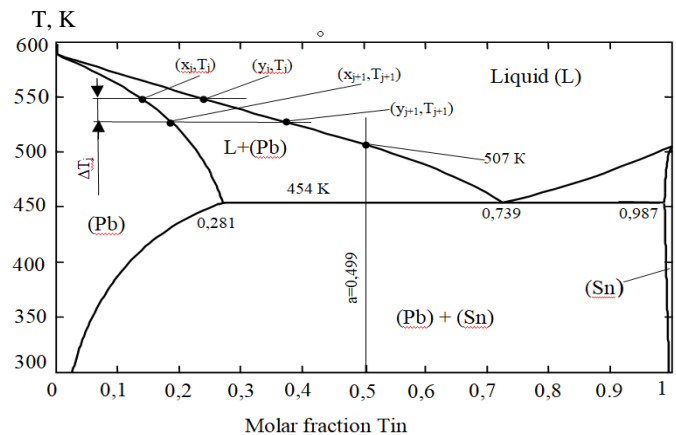


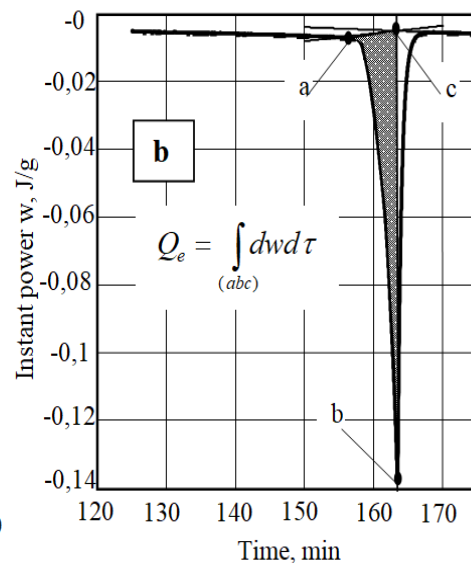
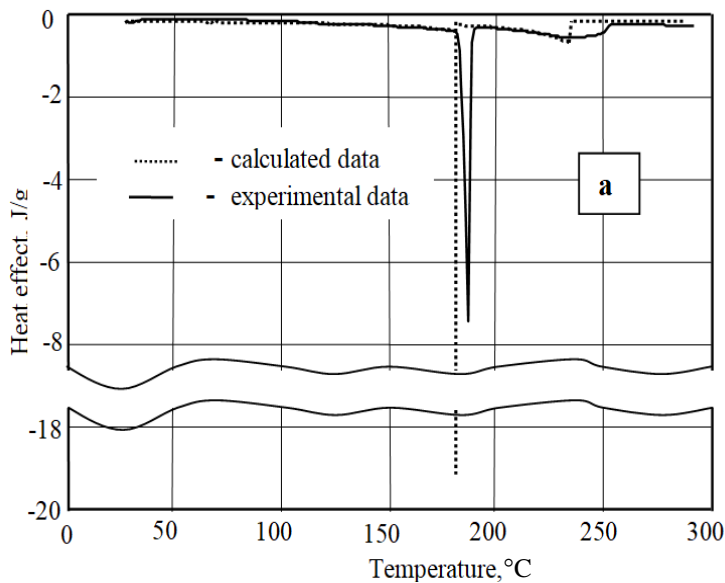
Fig. 1. Temperature dependences of specific heat effects when cooling the alloy Pb + 0.499 mol. of the fractions of Sn (a) and the scheme for determining the specific thermal effect during crystallization of the eutectic component of the alloy by the differential curve (b).

(1 - x), x - the content of plumbum and tin in the liquid phase (molar fractions); $\Delta H_i^{mix}(x, T)$ - change of the molar enthalpy of mixing in the phase when the temperature changes from T_j to T_{j+1} .

In the interval from the temperature of liquidus (507 K) to the eutectic temperature (454 K), and also at temperatures less than 454 K, the alloy stays in a two-phase state (Figure 1) (liquid phase + solid solution based on plumbum (Pb) - in the first case, and two solid solutions (Pb) + (Sn) - in the second case). To determine the changes of enthalpy in the process of cooling of the alloy in the two-phase regions of the system's existence, changes of the quantities and phases' constitutions when the temperature was changed by ΔT_j were taken into account:

Table 2. Temperature Dependences of Changes of Enthalpies (ΔH) and Heat Capacities (ΔC_p) of Components of Pb-Sn Systems at Phase Transitions

Component	Thermodynamic function	Type of phase transition I \rightarrow II		
		Liquid phase \rightarrow (Pb)	Liquid phase \rightarrow (Sn)	(Pb) \rightarrow (Sn)
Sn	$\Delta H^{I \rightarrow II}(T)$, J/moles	$-5622+0,055 \cdot T+0,012 \cdot T^2/2+1288342/T$	$-9168-3,952 \cdot T+0,0174 \cdot T^2/2+967769/T$	5510
	$\Delta C_p^{I \rightarrow II}(T)$, J/(moles·K)	$0,055+0,012 \cdot T-1288342/T^2$	$-3,952+0,0174 \cdot T+967769/T^2$	$-7,795 \cdot 10^{-13}+1,47 \cdot 10^{-13} \cdot T$
Pb	$\Delta H^{I \rightarrow II}(T)$, J/moles	-4700	$209555-1,408 \cdot T+0,00196 \cdot T^2/2-107767/T$	213580
	$\Delta C_p^{I \rightarrow II}(T)$ J/(moles·K)	0	$-1,408 \cdot T+0,00196 \cdot T^2/2+107767/T$	0

**Table 2.** Temperature Dependences of Changes of Enthalpies (ΔH) and Heat Capacities (ΔC_p) Components of Pb-Sn Systems at Phase Transitions

$$\Delta H_j = [H^I(x_{j+1}, T_{j+1})p_{j+1} + H^{II}(y_{j+1}, T_{j+1})q_{j+1}] - [H^I(x_j, T_j)p_j + H^{II}(y_j, T_j)q_j], \quad (12)$$

where $H^I(x_{j+1}, T_{j+1})$, $H^{II}(y_{j+1}, T_{j+1})$ are the molar enthalpies of phases I and II at temperatures T_{j+1} containing respectively x_{j+1} and y_{j+1} of molar fractions of tin (according to the diagram of the system's state); $H^I(x_j, T_j)$, $H^{II}(y_j, T_j)$ are the molar enthalpies of phases I and II at temperature T_j containing x_j and y_j of molar fractions of tin (according to the diagram of the system's state); p_{j+1} , p_j are the quantities of phase I, respectively, at temperatures T_{j+1} and T_j ; q_{j+1} , q_j are the quantities of phase II at temperatures T_{j+1} and T_j , respectively. The molar enthalpies of the phases were determined according to the proposed method. Changes of enthalpies and heat capacities of pure components at phase transitions (Table 2) were calculated from data on lattices' stability parameters [7]. The quantities and constitutions of phases remaining in equilibrium were calculated on the state diagram in accordance with the lever's rule.

At a temperature of 454 K, the alloy undergoes an eutectic transformation, which occurs at a constant temperature. Therefore, the change of enthalpy was calculated as the difference between the enthalpy of the liquid phase of the eutectic composition and of the sum of the enthalpies of two solid solutions, taking into account their quantities and compositions at eutectic temperature.

To verify the consistency of the proposed method with the help of differential scanning calorimetry, the temperature dependences of the thermal effects accompanying the cooling of the alloy of system Pb-Sn containing 0.499 mol of tin were empirically established (rate of temperature's change was 1K/min). It is established that the experimental and calculated data are in satisfactory compliance

(Figure 2a; for the convenience of comparison, the calculated data are given to 1 g of alloy, calorimetric data are in this form). For example, according to the calculations, the specific heat released during the crystallization of the alloy of the given composition is 40.93 J/g, while according to the experimental data, its value is 41.49 J/g (the difference does not exceed 1.5%). For the amount of heat released during the crystallization of the eutectic component of 1 g of alloy, these quantities are 19.29 J and 19.09 J, respectively (the difference does not exceed 1%). It should be noted that, due to the coherence of the dimensions, the temperature field is not homogeneous in terms of the volume of the sample under study. Therefore, the data on thermal effects on the experimental curves appear to be "stretched" along the abscissa axis (Figure 2a) and in order to exclude the influence of the inhomogeneity of the temperature field, the thermal effects at phase transitions were determined by the areas of figures bounded by peaks on the experimental differential curves and characteristic lines (Figure 2 b) [8].

4. Conclusions

1. A procedure for calculating of the temperature dependences of thermal effects accompanying the cooling and heating of multi-component alloys is developed. Their presence makes it possible to develop adequate mathematical models describing the crystallization of alloys of metallic systems.
2. The results of experimental verification indicate that the proposed method provides sufficient accuracy of calculation. The discrepancy between calculated values and experimentally obtained ones does not exceed 1.5%.

5. References

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