MATHEMATICAL MODELS OF CALCULATIONS OF PARAMETERS OF CRYSTALLIZATION OF BINARY ALLOYS BY MEANS OF COMPUTER THERMAL ANALYSIS

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Abstract: Mathematical models of crystallization of binary metal alloys crystallizing in the temperature range are proposed. These models are intended for use in the composition of quality control systems for cast alloys based on computer thermal analysis. The proposed models make it possible to calculate the time dependences of the relative amounts of the solid and liquid phases using the data of the cooling curve, as well as to determine the intensity of the increase of the amount of the solid phase. The method of determining the temperature dependences of the specific heat and latent crystallization heat using the data on the temperature-concentration dependences of the free energies of the phases forming the system under study was used.

KEYWORDS: *THERMAL ANALYSIS, CRYSTALLIZATION, ENTHALPHY, GIBBS ENERGY, HEAT CAPACITY*

1. Introduction

The final level of service properties of cast parts is laid down during the smelting and crystallization of alloys. It is at the stage of crystallization the "primary" structure of the solid metal is formed, which essentially determines the properties of the final product. Therefore, the creation of systems for operational control and management of the state of alloy, as well as control and management of crystallization phase of the melt is relevant.

The operation of many systems for monitoring of the state of metal melts is based on thermal analysis, which provides information on the thermal effects accompanying cooling of sample [1–7]. On the cooling curves (dependences of temperature on time T = f (t)), the thermal effects accompanying the formation of the cast metal structure are especially pronounced. Therefore, it seems promising studying the kinetics of crystallization and prediction of the service properties of metals in the solid state from the results of the analysis of cooling curves. The information which is obtained by this way (especially in the express mode) is necessary for making operational decisions on management of casting technological processes [5, 6].

In [8, 9], mathematical models were developed that describe the solidification of pure metals based on computer thermal analysis in the subsystem of quality control of casting melts. They describe the crystallization of a small sample of metal (for sufficiently small values of the Biot criterion: *Bi* << 1). When they were created, it was assumed that the specific heat (***c***) and latent heat of crystallization (***L***) are constants. Indeed, during the crystallization of pure metals, the specific latent heat of crystallization ***L*** is a constant value, while specific heat capacities of the liquid and solid phases differ (for example, for aluminum - by about 20%). It should be noted that these models were also used to describe the crystallization of alloys [8 - 10]. However, the crystallization of alloys occurs in the temperature range with changes in the composition of both the liquid and solid phases. Therefore, the values of the specific heat c and the specific latent heat of crystallization ***L*** depend on the composition and temperature of the liquid-solid medium, which, in turn, changes with time. Therefore, in the mathematical models of crystallization, intended for use in thermal analysis, it is necessary to make appropriate corrections.

The purpose of this work is to develop mathematical models of crystallization of multicomponent metal melts, which are crystallized in the temperature range, and are intended to interpret the results of computer thermal analysis.

2. Solution of the problem under consideration

Considering the solidification of a small casting, when the condition Bi << 1 is satisfied (which is typical for thermal analysis), we can write the heat balance equation [8]:

$$dQ = dQ_c + dQ_L, \qquad (1)$$

where dQ is the amount of heat given by the alloy to the environment; dQ_L - the amount of heat released as a result of the formation of a solid phase; dQ_C - the amount of heat released as a result of temperature changes during the cooling of the metal.

Such a record of the heat balance equation (1) assumes that the temperature gradient over the cross section of the casting is neglected, and the casting is a homogeneous material point with mass m_0.

In [6, 8 - 10], the well-known calorimetric relations were substituted in (1):

$$dQ_c = -cm_0 dT(t), \qquad (2)$$

$$dQ_L = Ldm(t), \qquad (3)$$

and the intensity (speed) of heat removal to the environment was described by the law of total heat transfer:

$$\frac{dQ}{dt} = fS\left[T(t) - T_e\right] + \sigma\varepsilon S\left[T^4(t) - T_e{}^4\right], \qquad (4)$$

where *T(t)* is the function of the dependence of the temperature of the metal sample on time (cooling curve of thermal analysis); T_e is the ambient temperature; ***c*** is the specific heat, ***L*** is the specific latent heat of crystallization; m_0 is the mass of the metal under study; *m(t)* is the mass of the metal which have been crystallized to the moment of time *t*; *f* is the heat transfer coefficient*; S* is the surface of the area from which heat is removed to the environment; ε - is the degree of blackness of the sample's surface; σ is the Stefan – Boltzmann constant.

Taking into account that the thermophysical parameters of alloys in the crystallization process are changed, it seems appropriate to determine the temperature-concentration dependences of the heat capacities of the phases $c(x,T(t))$ and the specific latent heat of crystallization $L(x,T(t))$ in the temperature range of crystallization for the particular alloy under study (here x is the content of the second component in the melt).

In [11], a method was proposed for determining of the dependences of interest from analytical expressions for the temperature-concentration dependences of the molar free energies of the phases. The calculation is based on the assumption that the values of enthalpy, entropy and isobaric-isothermal potential are interconnected through the heat capacity c_p:

$$\left.\begin{aligned} H &= \int c_p dT, \\ S &= \int \frac{c_p}{T} dT, \\ G &= H - TS = \int c_p dT - T\int \frac{c_p}{T} dT, \end{aligned}\right\} \qquad (5)$$

where G is the Gibbs free energy; H - is enthalpy; S - entropy.

For many metallic systems data on the temperature-concentration dependences of the Gibbs free energy of the phases forming the system under consideration are given in the literature. For example, for the case of a two-component system, the temperature-concentration dependence of the Gibbs molar energy of the phase is defined as:

$$G(x,T)=G_A(T)\cdot(1-x_B)+G_B(T)\cdot x_B + \\ + G_{mix}(x,T)+RT\cdot(x_A\ln x_A + x_B \ln x_B), \quad (6)$$

where $G_A(T)$, $G_B(T)$ are the molar free energies of the pure components *A* and *B* in the phase at temperature *T;* , $x_A=1-x_B$, x_B - are content of components *A* and *B* in the phase (molar fractions); $G_{mix}(x,T)$ - is excess molar free energy of mixing in the phase of composition x at temperature T ; R - is the universal gas constant.

If the temperature-concentration dependence of the molar heat capacity $c_P(x,T)$ of the phase is expressed as a polynomial

$$c_p(x,T)=z_3(x)+z_4(x)T + \\ + \frac{z_5(x)}{T^2}+z_6(x)T^2+z_7(x)T^3+\dots \ , \quad (7)$$

then, in accordance with (5):

$$G(x,T)=z_1-z_2T+z_3(x)T(1-\ln T)- \\ + \frac{z_4(x)T^2}{2}-\frac{z_5(x)}{2T}-\frac{z_6(x)T^3}{6}-\frac{z_7(x)T^4}{12}+\dots \ , \quad (8)$$

where z_1 and z_2 are the integration constants.

The dependence of the heat capacity on the composition can be taken into account by presenting the coefficients in (7) in the form of polynomials

$$z_k(x)=z_{k,1}(x)+z_{k,2}(x)x+z_{k,3}(x)x^2+\dots \quad (9)$$

Therefore, by presenting the temperature-concentration dependences of the free energies of the phases (6) in the form of polynomials (8) (for example, using the polynomial regression), one can obtain the desired temperature-concentration dependences of the heat capacities of the phases $c(x,T(t))$.

Taking into account (5), the temperature-concentration dependences of the enthalpies of the phases take the form:

$$H(x,T)=z_1+z_3(x)T+\frac{z_4(x)T^2}{2}- \\ -\frac{z_5(x)}{T}+\frac{z_6(x)T^3}{3}+\frac{z_7(x)T^4}{4}+\dots, \quad (10)$$

Changes of the enthalpy of the system during the transition from the melt to the solid solution, calculated as the difference between the enthalpies of the liquid and solid phases (taken with the appropriate sign), are nothing else but the desired temperature-concentration dependences of the specific heat of crystallization $L(x,T(t))$.

Having determined by this way the temperature-concentration dependences $c(T(t))$ and $L(T(t))$ and substituting them in (2) and (3), equation (1) can be reduced to the form:

$$\frac{dV(t)}{dt}=\frac{c(T(t))}{L(T(t))}\frac{dT(t)}{dt}+\frac{k_{co}}{L(T(t))}\left[T(t)-T_e\right]+ \\ + \frac{k_{ra}}{L(T(t))}\left[T^4(t)-T_e^4\right], \quad (11)$$

$$V(t)=\frac{m(t)}{m_0}, \quad (12)$$

$$k_{co}=\frac{fS}{m_0}, \quad (13)$$

$$k_{ra}=\frac{\sigma\varepsilon S}{m_0}, \quad (14)$$

where $V(t)$ is the relative amount of solids.

The solution of equation (11) can be obtained by direct integration:

$$V(t)=\int_w^t\frac{c(T(t))}{L(T(t))}\frac{dT(t)}{dt}dt+\int_w^t\frac{k_{co}}{L(T(t))}\left[T(t)-T_e\right]dt+ \\ + \int_w^t\frac{k_{ra}}{L(T(t))}\left[T^4(t)-T_e^4\right]dt. \quad (15)$$

The under integral functions in (15) are complex non-linear dependencies. However, taking into account the fact, that the result of thermal analysis is the cooling curve $T(t)$, which is a time series with constant time intervals [9], the integrals in expression (15) are easily calculated by numerical methods. The calculation uses the initial condition:

$$V(t_{cr})=0, \quad (16)$$

showing the absence of a solid phase at the onset of crystallization.

3. Results and discussion

The proposed mathematical model (16) allows to determine the amount of the solid phase $V(t)$ at any time of crystallization using the cooling curve obtained by thermal analysis. Although the same information can be obtained from the alloy state diagram, due to the non-equilibrium crystallization conditions, its use leads to significant calculation inaccuracies. Beside this, the usage of a state diagram does not allow to estimate the intensity (rate) of the formation of a solid phase $V'(t)$. But this is namely that parameter which is used for prediction of mechanical properties of alloys [5, 6].

For practical calculations of the amount of the solid phase and the intensity of its formation using expressions (11) and (16), first of all it is necessary to determine the time derivative of the temperature $T'(t)$ from the cooling curve and calculate the coefficients k_{co} and k_{ra}. Calculation of $T'(t)$ is easily implemented using the numerical differentiation formulas. However, in many cases, pre-filtering of the cooling curve is required [9]. To determine the values of the coefficients k_{co} and k_{ra} from the cooling curve, one can use the method of determining of the coefficients k_1 and k_2, given in [9]. In [9], they are calculated by linearizing the portions of the cooling curve before and after crystallization, followed by the using of the least squares method. The coefficients k_{co} and k_{ra} are related to k_1 and k_2 as follows:

$$k_{co}=k_1c_{Li}, \quad (11)$$

$$k_{ra}=k_1c_{So}, \quad (12)$$

where c_{Li} , c_{So} are the specific heat values of the studied alloy in the liquid and solid states.

The above mentioned methodology can also be used in the development of mathematical models of crystallization of alloys with eutectic. Models for such alloys are given in [10], where temperature dependences of thermal parameters are not taken into account.

4. Conclusions

In this paper, we developed a method for constructing of

mathematical models of crystallization of binary metal alloys which are crystallized in the temperature range. A characteristic feature of the proposed models is to take into account the dependence of the specific heat and latent heat of crystallization on temperature. For this purpose, the temperature-concentration dependences of the free energies of the phases forming the system under study are used. The proposed models make it possible to calculate the time dependences of the relative amounts of the solid and liquid phases from the cooling curves obtained by using of computer thermal analysis, as well as to determine the intensity of formation of the solid phase.

5. References

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