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THERMAL MODEL "MELT–NUCLEUS" AND STUDY OF THE CHARACTERISTICS OF THE TRANSITION ZONE UNDER THE EFFECT OF THE ELECTRONIC STRUCTURE OF THE 3*d*-ELEMENTS IN ALUMINUM

A. N. Chichko and Yu. V. Yatskevich

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On the basis of the model thermal parameters of the transition zone "aluminum melt–3d-nucleus" it is shown that a change in the degree of filling has two extrema that are related to d^5 and d^{10} states.

A mathematical simulation of the process of nucleation in melts is one of the most disputable and less studied problems of the theory of crystallization [1]. An insufficient study of electronic mechanisms of nucleation is the "heel of Achilles" of the theory of crystallization, thus making it impossible to predict the character of crystallization on introduction of elements of various electronic structures to the melt. This results in the fact that information about the process of crystallization of alloys at a microlevel to a great extent lags behind similar data obtained at the macrolevel. Thus, in spite of a large number of publications devoted to thermal calculations [2, 3], works on the study of the effect of the electronic structure of the components of the alloy on the parameters of thermal models are virtually absent.

We studied the interrelations between the model parameters obtained on the basis of the equation of heat conduction for the aluminum melt–nucleus of 3*d*-element system and the electronic structure of the nucleus.

In calculation of temperature-time dependences (TTD) we used a three-dimensional differential equation of heat conduction [4]

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{c\rho}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{F}{c\rho}. \tag{1}$$

With account for the dependence of thermal conductivity and heat capacity of the material on temperature Eq. (1) has the form

$$\frac{\partial T}{\partial \tau} = \frac{1}{c(T)\rho}\left(\frac{\partial\left(\lambda(T)\dfrac{\partial T}{\partial x}\right)}{\partial x} + \frac{\partial\left(\lambda(T)\dfrac{\partial T}{\partial y}\right)}{\partial y} + \frac{\partial\left(\lambda(T)\dfrac{\partial T}{\partial z}\right)}{\partial z}\right) + \frac{F}{c(T)\rho}. \tag{2}$$

$T(\tau)$ was determined from Eq. (2) on the basis of the finite-difference scheme [5], in which the volume was divided to cubic elements with a length $\Delta x = 1$ cm, a width $\Delta z = 1$ cm, and a height $\Delta y = 1$ cm. The temperature increment in one element in the interval of time $\Delta\tau = 0.25$ sec was determined by the formula

$$\Delta T_{x,y,z} = \frac{\Delta\tau}{c(T)\rho} \times$$

$$\times \left(\frac{\lambda\left(\dfrac{T_{x,y,z} + T_{x+\Delta x,y,z}}{2}\right)\dfrac{T_{x+\Delta x,y,z} - T_{x,y,z}}{\Delta x} - \lambda\left(\dfrac{T_{x,y,z} + T_{x-\Delta x,y,z}}{2}\right)\dfrac{T_{x,y,z} - T_{x-\Delta x,y,z}}{\Delta x}}{\Delta x} + \right.$$

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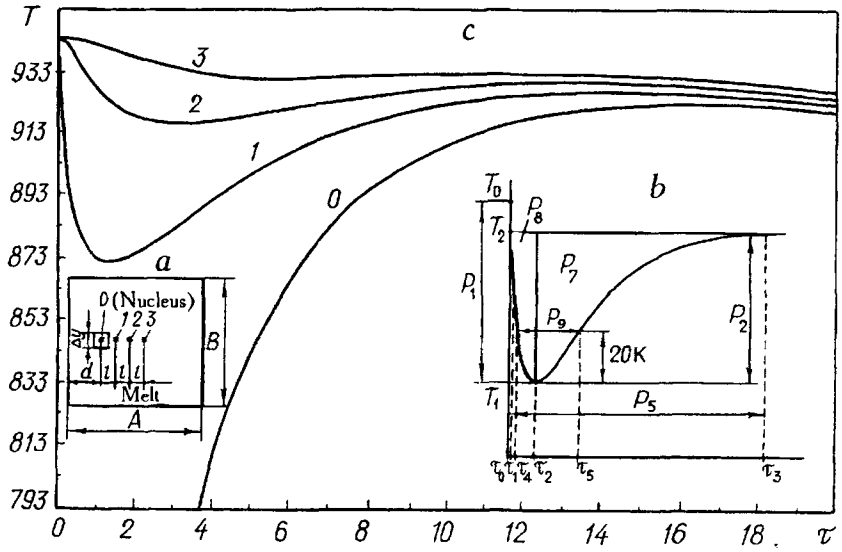

Fig. 1. Schematic of the thermal system "melt–nucleus" (a), scheme of the calculation of the parameters of the transition zone (b), and temperature-time dependence of the aluminum melt–nickel nucleus system (c). T, K; τ, sec.

$$+\frac{\lambda\left(\frac{T_{x,y,z}+T_{x,y+\Delta y,z}}{2}\right)\frac{T_{x,y+\Delta y,z}-T_{x,y,z}}{\Delta y}-\lambda\left(\frac{T_{x,y,z}+T_{x,y-\Delta y,z}}{2}\right)\frac{T_{x,y,z}-T_{x,y-\Delta y,z}}{\Delta y}}{\Delta y}+$$

$$+\frac{\lambda\left(\frac{T_{x,y,z}+T_{x,y,z+\Delta z}}{2}\right)\frac{T_{x,y,z+\Delta z}-T_{x,y,z}}{\Delta z}-\lambda\left(\frac{T_{x,y,z}+T_{x,y,z-\Delta z}}{2}\right)\frac{T_{x,y,z}-T_{x,y,z-\Delta z}}{\Delta z}}{\Delta z}+$$

$$+F(x, y, z)\,\Delta x\,\Delta y\,\Delta z\Bigg), \tag{3}$$

and a volumetric density of the power in crystallization by the relation

$$F(x, y, z)=\begin{cases}\left(1-\dfrac{Q_{x,y,z}}{Q_{\mathrm{cr}}}\right)\xi, & \text{if } T_{x,y,z}<T_{\mathrm{cr}},\\ -\dfrac{Q_{x,y,z}}{Q_{\mathrm{cr}}}\,\xi, & \text{if } T_{x,y,z}>T_{\mathrm{cr}},\end{cases} \tag{4}$$

where $Q_{x,y,z}$ – the amount of heat released in the element with the coordinates (x, y, z) – changes with each tact by the formula

$$Q_{x,y,z}(\tau+\Delta\tau)=Q_{x,y,z}(\tau)+F(x, y, z)\,\Delta x\,\Delta y\,\Delta z. \tag{5}$$

TTDs of the systems "aluminum melt–nucleus of X-element" (where X is Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) were calculated by (3)-(5) using the initial conditions (T_0 = 943 K for the melt, T_0 = 293 K for the nucleus, T_0 = 293 K for the mold, for 1 cm^3 of aliminum Q_{cr} = 914 J, T_{cr} = 933 K). The system changes in accordance with a sequential increase in the degree of filling of $s + d$ electrons of $3d$-elements that are the nuclei in the aluminum melt.

Figure 1a presents a model scheme of the melt–nucleus system. In the calculations we used the following parameters of the solid and liquid phases: A = 30 cm, B = 30 cm, d = 5 cm, l = 1 cm. The heat capacity of the mold

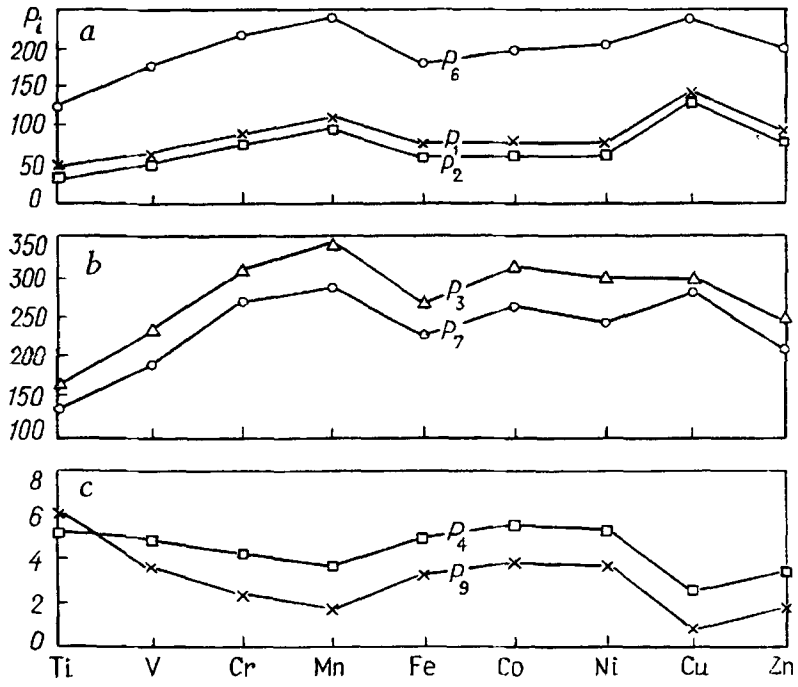

Fig. 2. Influence of the electronic structure of the nucleus on the parameters of the temperature-time dependence P_1, K; P_2, K; P_3, K·sec; P_4, sec; P_6, ×10 K; P_7, K·sec; P_9, sec (calculation for point 1, Fig. 1a).

is $5 \cdot 10^5$ J/(m^2·K); its thermal conductivity is 5 W/(m·K). It should be noted that a qualitative picture of the governing laws given below does not depend on the above-described characteristics. It is seen from Fig. 1c that the process of heating characterized by an increase of temperature occurs at point 0. At point 3 the temperature decreases with time. At points 1 and 2 the "effect of supercooling," characterized by the change in the sign of the derivative $dT(\tau)/d\tau$, is observed on the TTD. The distinguishing portion of the TTD (Fig. 1b) characterizes thermal processes of the transition zone "melt–nucleus." The following parameters of the TTD for the "aluminum melt–nucleus of 3d-element" systems were calculated for this portion:

$$P_1 = T_0 - T_1\,,\quad P_2 = T_2 - T_1\,,\quad P_3 = T_3(\tau_3 - \tau_1) - \int_{\tau_1}^{\tau_3} T(\tau)\,d\tau\,,$$

$$P_4 = P_3/P_2\,,\quad P_5 = \tau_3 - \tau_1\,,\quad P_6 = P_3/P_5\,,$$

$$P_7 = T_3(\tau_3 - \tau_2) - \int_{\tau_2}^{\tau_3} T(\tau)\,d\tau\,,\quad P_8 = T_3(\tau_2 - \tau_1) - \int_{\tau_1}^{\tau_2} T(\tau)\,d\tau\,,\quad P_9 = \tau_4 - \tau_5\,.$$

All the listed parameters correspond to the change of the temperature at point 1 (Fig. 1a), i.e., thermal conditions of cooling melt with the model nucleus are the same for all 3d-elements, thus making it possible to estimate the effect of the degree of filling of the electronic shell of the atoms of the nucleus.

Figure 2 presents the calculated data on the effect of the degree of filling of the electronic shell of the atoms of the nucleus on the parameters of the TTD of the transition zone of the system "aluminum melt–nucleus of 3d-element." As is seen from Fig. 2a, the parameters P_1, P_2, P_6 have a tendency to maximization in the systems "aluminum melt–manganese" and "aluminum melt–copper." At the same time the higest values of the coefficient of thermal conductivity are observed for manganese and copper (W/(m·K) at 873 K): $\lambda^{Mn} = 127$, $\lambda^{Cu} = 373$ compared to $\lambda^{Ti} = 21$, $\lambda^{V} = 37$, $\lambda^{Cr} = 70$, $\lambda^{Fe} = 35$, $\lambda^{Co} = 44$, $\lambda^{Ni} = 50$, $\lambda^{Zn} = 90$. Comparing these data and changes in the parameters we can assume that P_1, P_2, P_6 characterize physical properties connected with the difference in the coefficients of thermal conductivity of aluminum and the 3d-element.

As is seen from Fig. 2b, it is general for the parameters P_3, P_7 to also have a tendency to maximization in the systems with manganese. At the same time, for the elements with intermediate configurations of the range $d^5 < X < d^{10}$ (d^6s^2(Fe), d^7s^2(Co), d^8s^2(Ni), $d^{10}s^1$(Cu)) one maximum is observed: in the aluminum–cobalt system for the parameter P_3, and in the aluminum–copper system for the parameter P_7. It should be noted that the transitions Ti → V → Cr → Mn (Fig. 2b) are characterized by the highest thermal conductivity at Mn (c_V(873 K) = $4.79 \cdot 10^6$ J/(m^3·K)). The data on the properties of thermal insulation are taken from [6]. A similar maximization with cobalt is observed with a change in heat capacity with inverse transitions (J/(m^3·K) at 873 K): Zn ($c_V = 3.43 \cdot 10^6$) → Cu ($c_V = 3.96 \cdot 10^6$) → Ni ($c_V = 4.85 \cdot 10^6$) → Co ($c_V = 5.26 \cdot 10^6$).

Figure 2c presents data of the calculation of the effect of 3d-elements on the parameters P_4 and P_9. In this case the minimization of these parameters on the transitions Ti → V → Cr → Mn is observed for the aluminum–manganese system; this can be attributed to a decrease in the ratios (sec/m^2 at 873 K) $c_V^{Ti}/\lambda^{Ti} = 13.8 \cdot 10^4$, $c_V^{V}/\lambda^{V} = 9.7 \cdot 10^4$, $c_V^{Cr}/\lambda^{Cr} = 6.4 \cdot 10^4$, $c_V^{Mn}/\lambda^{Mn} = 3.8 \cdot 10^4$.

Comparing the changes in the parameters P_4 and P_9 with the changes in the ratio c_V(873 K)/λ(873 K) for the systems with intermediate configurations d^6s^2, d^7s^2, d^8s^2, $d^{10}s^1$ we can see the shift of the maximum from Co to Fe ((sec/m^2 at 873 K): Cu ($c_V/\lambda = 1.1 \cdot 10^4$) → Ni ($c_V/\lambda = 9.7 \cdot 10^4$) → Co ($c_V/\lambda = 12 \cdot 10^4$) → Fe ($c_V/\lambda = 13.1 \cdot 10^4$) → Mn ($c_V/\lambda = 3.8 \cdot 10^4$)).

Thus, an analysis of the TTD of the transition zone of the aluminum melt–nucleus of the 3d-element system shows that the tendency of the element 3d to form d^5 and d^{10} electronic configurations leads to maximization of the parameters P_1, P_2, P_3, P_6, P_7 and minimization of P_4, P_9. For the systems with nuclei of the elements 3d characterized by a spectrum of intermediate configurations P_i changes with the transitions Ti → V → Cr → Mn and Cu → Ni → Co → Fe. This indicates the effect of the degree of filling of the electron shell of the nucleus on a thermal model of crystallization. The parameters of the TTD which characterize the depth of "supercooling" (P_1, P_2, P_6) correlate with thermal conductivity of the nucleus and are maximum for the systems with the largest weight of d^5 and d^{10} electronic states. The effect of the nuclei characterized by these configurations is likely to be caused by an increase in the phonon component of thermal conductivity in the system. The parameters of the TTD characterizing the length of the zone of "supercooling" (P_3, P_4, P_5, P_7, P_9) are to a larger extent associated with heat capacity of the nucleus and are maximum for the configurations d^5. With a change in the temperature the second maximum for them can shift from the states d^{10} toward the states d^5.

Comparing the results obtained with the data on the change in the limit of solubility, the eutectics point, and other characteristics of the aluminum–3d-element system [7], we can note that they fall within a general picture of the configuration model of the growth of nuclei [8]. The presence of two extrema in the properties of the liquid-solid state – one in the aluminum–manganese alloys, the other in one of the alloys the doping element of which has a configuration within the range $d^5 < X < d^{10}$ – is typical of the aluminum systems.

Thus, with change in the degree of filling of electrons of the nucleus in transitions Ti → V → Cr → Mn → Fe → Co → Ni → Cu → Zn thermal parameters of the transition zone "aluminum melt–nucleus of 3d-element" have two extrema, which are associated with maximization of the states d^5 and d^{10}.

NOTATION

T, temperature; T_0, T_{cr}, initial temperature, temperature of crystallization; x, y, z, Cartesian coordinates; $T_{x,y,z}$, temperature of the liberated element with the coordinates (x, y, z); Δx, Δy, Δz, dimensions of the element of the modeled space; τ, $\Delta\tau$, time and tact of modeling; $T(\tau)$, temperature-time dependence; τ_1, τ_2, τ_3, times corresponding to critical temperatures T_1, T_2, T_3; $\tau_4 < \tau_2$, $\tau_5 > \tau_2$, times for T_2 + 20 K; λ, c, ρ, coefficient of thermal conductivity, specific heat capacity, density of the material; $c_V^{Ti}(T)$, $c_V^{V}(T)$, $c_V^{Cr}(T)$, $c_V^{Mn}(T)$, $c_V^{Fe}(T)$, $c_V^{Co}(T)$, $c_V^{Ni}(T)$, $c_V^{Cu}(T)$, $c_V^{Zn}(T)$, heat capacity of the unit volume of the corresponding metal at temperature T; $\lambda^{Ti}(T)$, $\lambda^{V}(T)$, $\lambda^{Cr}(T)$, $\lambda^{Mn}(T)$, $\lambda^{Fe}(T)$, $\lambda^{Co}(T)$, $\lambda^{Ni}(T)$, $\lambda^{Cu}(T)$, $\lambda^{Zn}(T)$, coefficient of thermal conductivity of the corresponding metal at temperature T; F, volumetric density of the power of liberation or absorption of heat in crystallization or melting, respectively; Q_{cr}, maximum amount of heat liberated in crystallization of metal in the volume $\Delta x \Delta y \Delta z$; ξ, empirical coeffcient determined for the given metal; P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9, parameters of the

temperature-time dependence; A, B, dimensions of the liquid phase; d, l, distance from the nucleus to the boundary of the liquid phase and distance between the points of taking temperature-time dependences.

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