

Solidification of the Eutectic Ga–Sn Alloy

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Abstract—Cyclic thermal analysis is used to study the effect of overheating of the eutectic Ga–8.5 mol % Sn melt on the presolidification supercooling. It is found that, when the liquid eutectic is overheated above the eutectic temperature ($T_e = 293.5$ K) and is subsequently cooled, the dependence of the presolidification supercooling on the overheating temperature exhibits monotonic ascending behavior. The maximum supercooling after heating of the melt to 339 K is 26 K. The kinetic and thermodynamic parameters of eutectic solidification are calculated using the thermal analysis curves measured during melting.

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INTRODUCTION

Low-melting gallium-based alloys, in particular those with tin, are widely used in manufacturing semiconductor products and solar cells for light current sources; in laser, superconducting, high-vacuum, and nuclear engineering; for the production of low-temperature solders and glues; for the correction of pouring defects in glass and ceramics industries; for manufacturing lubricants; and in stomatology [1–4]. The eutectic Ga–Sn alloy is used for manufacturing metallic mercury-free stamps [5]. Moreover, this alloy affects the phase formation in multicomponent systems [6]. The efficiency of application of eutectic alloy is determined by its preparation procedure and solidification conditions. These conditions depend to a large extent on the thermal history of the liquid phase [7]. In particular, depending on the heating temperature of liquid, the solidification of gallium [8] and tin [9] during subsequent cooling can occur in two ways, namely, equilibrium solidification (ES) without supercooling and nonequilibrium solidification (NES) with a certain (for each metal) supercooling. Analogous regularities are likely to be expected for the eutectic alloy, since the structure and properties of the solid phase depend on the way of solidification.

According to the Ga–Sn phase diagram [10] (Fig. 1), the eutectic temperature for the eutectic (E) composition Ga–8.5 mol % Sn is $T_e = 293.5$ K. The hypoeutectic region is characterized by the existence of a Ga-based α solid solution; the hypereutectic region is represented by a tin-based β solid solution. Thus, the eutectic alloy below the eutectic temperature is a mixture of α and β solid solutions.

EXPERIMENTAL

Cyclic thermal analysis (CTA) [11] is used to study the effect of overheating ΔT^+ of the 91.5 mol % Ga–8.5 mol % Sn eutectic melt ($\Delta T^+ = T - T_e$, $T > T_e$) above eutectic temperature T_e on supercooling ΔT_e^- ($\Delta T_e^- = T_e - T_{\min}$, where $T_{\min}$ is the minimum temperature in the supercooling range at which solidification starts).

Eutectic compositions 0.5 g in mass were prepared by melting of special purity grade gallium and tin. The components were heated in an alundum crucible to

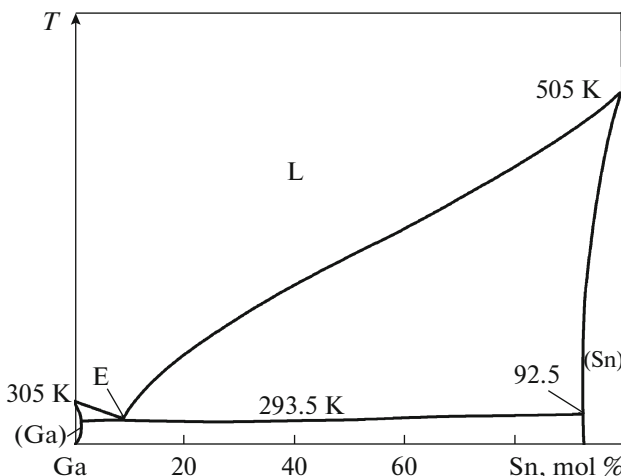


Fig. 1. Ga–Sn phase diagram [10].

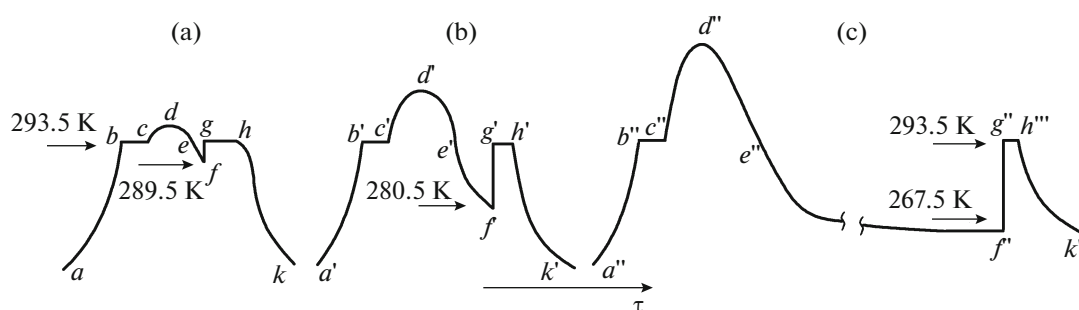


Fig. 2. Schematic heating and cooling curves for the eutectic alloy, which indicate an increase in the supercooling with the preliminary overheating; $cb = c'b' = c''b'' = 2.4$ min.

555 K, i.e., above the melting temperature of tin (505 K) and gallium (305 K), and mixed to their complete dissolution. Thermal cycling of all (five) samples was performed under the same conditions using the so-called gradient-free resistance furnace specially designed for cyclic thermal analysis. The furnace with a sample was located in a Veko cooling chamber at a temperature of 249 K. The temperature was measured with a chromel–alumel thermocouple using a UT325 digital thermometer interfaced with a computer. The thermocouple was lowered directly into the melt through a protective thin cylindrical quartz capsule. The error of measuring the temperature was ~ 0.1 K. Cyclic thermal analysis consisted in continuous recording the temperature during cyclic heating and cooling in the temperature (T)–time (τ) coordinates in a temperature range of 249–473 K, which covers temperatures 100 K above and 45 K below eutectic transformation temperature T_e . The lower temperature (249 K) was unchanged, whereas the upper temperature was progressively increased by 2–3 K relative to that of the preceding cycle. The heating rate was 3–4 K/min. During cooling, the furnace (and sample) temperature was decreased at a rate of 6.0–0.05 K/min in accordance with the exponential law $T = T_0 \exp(-\alpha\tau)$, where T_0 is the temperature at the onset of cooling and α is a constant.

RESULTS AND DISCUSSION

In the course of CTA of the Ga–8.5 mol % Sn eutectic alloy, a number of endo- and exothermic effects and regularities were found near the eutectic temperature.

Figure 2 shows some schematic heating–cooling curves for the eutectic alloy, which were plotted on coordinates T – τ and demonstrates that presolidification supercooling ΔT_e^- increases as melt overheating ΔT^+ increases.

During heating of a sample, the curves from points a (a' , a'') to points d (d' , d'') demonstrate horizontal portions bc' ($b'c'$, $b''c''$) at a temperature of 293.5 ± 0.5 K,

which corresponds to eutectic temperature T_e . It should be noted that, in all cycles, the melting time τ_m of the eutectic 0.5 g in mass was unchanged and equal to 2.4 min.

An analysis of the CTA curves (Figs. 2a–c) from points d (d' , d'') to points k (k' , k'') allowed us to reveal presolidification supercooling ΔT_e^- near points e (e' , e'')– f (f' , f''). No supercooling was observed only after a slight overheating of the melt to ~ 0.5 K. In this case, quasi-equilibrium solidification at T_e takes place. After overheating ΔT^+ of the eutectic melt above T_e and subsequent cooling, an increase in supercooling ΔT_e^- to 26 K was observed. In particular, an overheating of $\Delta T^+ = 9$, 15, and 34 K corresponds to a supercooling of $\Delta T_e^- = 4$, 13, and 26 K, respectively. The subsequent overheating of liquid eutectic above T_e from 34 to 100 K weakly affects average supercooling $\langle \Delta T_e^- \rangle$, which is ~ 26 K. This supercooling can be considered as maximum $\Delta T_{\max}^-$ under our experimental conditions.

Thus, after heating of the liquid eutectic to any temperatures above T_e and subsequent cooling, solidification always occurs with presolidification supercooling ΔT_e^- and exhibits a nonequilibrium explosive character at the initial stage. This is indicated by the rapid increase in the temperature from the temperature corresponding to point f (f' , f'') to T_e at a rate of 30–40 K/s. The subsequent solidification along path gh ($g'h'$, $g''h''$) is equilibrium at T_e .

Figure 3 shows the general dependence of ΔT_e^- on ΔT^+ for the eutectic alloy, which was plotted using about 100 heating–cooling cycles. The averaged supercooling scatter relative to average magnitudes for all thermal cycles for five samples was ± 2 K.

For comparison, Fig. 3 shows ΔT^- versus ΔT^+ for gallium and tin [8, 9]. The dependence for tin is described by Heaviside function

$$\Delta T^- = \langle \Delta T_{\max}^{\text{Sn}} \rangle \Theta(\Delta T^+ - \Delta T_{\text{cr}}^+),$$

$$\Theta = \begin{cases} 1, & \Delta T^+ > \Delta T_{\text{cr}}^+, \\ 0, & \Delta T^+ \leq \Delta T_{\text{cr}}^+, \end{cases} \quad (1)$$

$$\Delta T_{\text{cr}}^+ = 5 \text{ K}, \quad \Delta T_{\max}^{\text{Sn}} = 10 \text{ K}.$$

In Eq. (1), ΔT_{cr}^+ is the critical overheating of the tin melt, after which the character of solidification changes stepwise from ES to NES. After cooling of the overheated melt from ΔT_{cr}^+ or higher temperatures, nonequilibrium solidification with supercooling is observed; in the case of underheating of the melt to ΔT_{cr}^+ and subsequent cooling, solidification is equilibrium without supercooling [9].

This dependence for gallium has the form

$$\Delta T_L^- = \frac{\Delta T_{\max}^{\text{Ga}}}{1 + \exp[-a(\Delta T^+ - b)]}, \quad (2)$$

where $\Delta T_{\max}^{\text{Ga}} = 34 \text{ K}$, $a = 0.36 \text{ K}^{-1}$, and $b = 8 \text{ K}$.

Finally, the aforementioned dependence for the eutectic alloy has the form

$$\Delta T_e^- = \frac{\Delta T_{\max}^{\text{E}}}{1 + \exp[-c(\Delta T^+ - d)]}, \quad (3)$$

where $\Delta T_{\max}^{\text{E}} = 26 \text{ K}$, $c = 0.28 \text{ K}^{-1}$, and $d = 6.0 \text{ K}$.

It is seen that the dependence of ΔT_e^- on ΔT^+ is continuous for the eutectic alloy (Eq. (3)) and gallium (Eq. (2)) and discontinuous (steplike) for tin.

In addition to the supercooling, the following parameters were determined from the thermal curves of the eutectic: the time of residence of the melt in the supercooled state (τ_1), i.e., the time required for temperature to pass from point e to point f' (or $e' \rightarrow f'$ and $e'' \rightarrow f''$); the time of rapid increase in the temperature (τ_2) in the range of points $f(f', f'')$ and $g(g', g'')$; and the time calculated from the length of solidification plateau $gh(g'h', g''h'')$ in Fig. 2 (τ_3).

According to the cluster-coagulation solidification model [7], τ_1 is the time of formation of crystal nuclei and crystal-like clusters in the supercooled melt; τ_2 is the time of coagulation of these structural elements, which results in the formation of the initial fraction of solid $\eta = m_x/m$ in mass m_x , where m is the mass of the entire sample (in thermal analysis curves, this is the time of a rapid increase in the temperature from $T_{\min}$ to T_e , which is the evidence of a certain adiabatic process in the supercooled melt; the mechanism of this phenomenon is poorly understood); and τ_3 is the time of solidification of the rest of sample $1 - \eta$. Thus, the

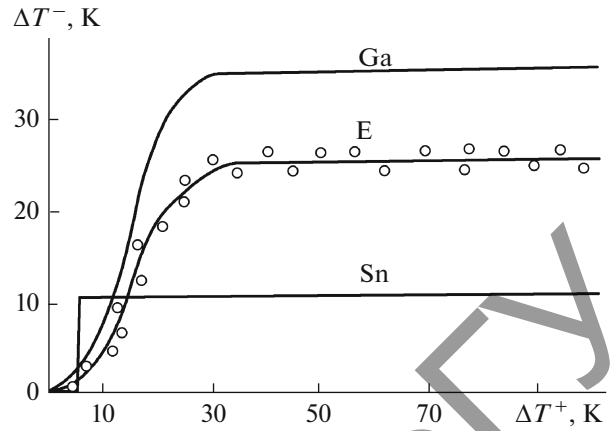


Fig. 3. Supercooling ΔT^- vs. overheating ΔT^+ for the gallium, tin, and Ga–8.5 mol % Sn (eutectic E) melts.

total time of solidification of the entire sample can be represented as the sum $\tau = \tau_1 + \tau_2 + \tau_3$. Incubation period τ_1 increases according to an exponential law as the cooling rate decreases and reaches, for example, 13 min for the curve in Fig. 2c. Time τ_2 varies depending on the cooling rate and the supercooling; for the curve in Fig. 2c, we have $\tau_2 \approx 1 \text{ s}$.

Based on the curves given in Fig. 2, we can assume that, during solidification of the portion of sample of mass m_x in time τ_2 , latent heat $Q_1 = \Delta H_{LS} m_x$ is released and heats the entire sample from the temperature $T_{\min}$ (points f, f', f'') to T_L (points g, g', g''). In this case, heat $Q_2 = c_p m \Delta T_e^-$ is used. Since $\tau_2 \ll \tau_1, \tau_3$, the heat losses in time τ_2 can be neglected. In this case, using the heat balance equation $Q_1 \approx Q_2$, we can calculate the fraction η of eutectic E solidified in τ_2 from the m_x -to- m mass ratio,

$$\eta = m_x/m = c_p^{\text{E}} \Delta T_e^- / \Delta H_e, \quad (4)$$

where c_p^{E} is the additive heat capacity of the eutectic (398.64 J/(kg K)) and ΔH_e is the enthalpy of eutectic solidification (72.77 J/kg).

The calculations performed by Eq. (4), for example, for $\Delta T_e^- = 4, 13$, and 26 K give $\eta = 0.025, 0.07$, and 0.14 , respectively.

Obviously, τ_3 is the time of subsequent isothermal solidification of the rest of the melt ($1 - \eta$). In all cycles, it was almost the same ($\sim 2 \text{ min}$) and always shorter than the melting time (2.4 min).

η at different supercoolings depends also on the time of residence of the melt in the supercooled state (τ_1). When accepting that η is the concentration of crystal-like clusters and nuclei that form in the supercooled area in time $0 < t < \tau_1$, the Avrami–Kolmogorov equation $\eta = 1 - \exp(-Zt^n)$ can be used for deter-

Activities a_e^{Ga} , a_e^{Sn} , α_e^{Ga} , α_e^{Sn} , coefficients of activity g_e^{Ga} , g_e^{Sn} , γ_e^{Ga} , and γ_e^{Sn} and activation energies W_e^{Ga} , W_e^{Sn} , ω_e^{Ga} , and ω_e^{Sn} in the liquid eutectic and its enthalpy of melting (kJ/mol)

Parameter	Parameter at $\Delta T_{\text{max}}^{\text{E}}$, K	
	0	26
a_e^{Ga}	0.93200	—
a_e^{Sn}	0.29960	—
g_e^{Ga}	1.0085 (1.0193)	—
g_e^{Sn}	3.4823 (3.4950)	—
α_e^{Ga}	—	0.9735
α_e^{Sn}	—	0.2299
γ_e^{Ga}	—	2.7047 (2.1329)
γ_e^{Sn}	—	1.0639 (0.8202)
W_e^{Ga}	—3.63	—
W_e^{Sn}	—6.29	—
ω_e^{Ga}	—	—5.97
ω_e^{Sn}	—	—14.4
ΔH_L	—7.07 (Sn)	—5.59 (Ga)

mining nucleation constant Z and Avrami parameter n . The Avrami parameter $n \approx 1.25$ was determined by log–log transformation, plotting the dependence of $y = \ln \ln(1/(1 - \eta))$ on $x = \ln t$, and using the slope $\tan \varphi = y(x)$ [1]. Under these conditions, the nucleation constant is $Z \approx 7.4 \times 10^{-2}$.

Two components (Ga, Sn) participate in the eutectic solidification; because of this, their activities in the eutectic both at T_e , i.e., at the onset of equilibrium solidification and in the supercooling range at T_{min} at the onset of nonequilibrium explosive solidification, should be calculated.

The activities of gallium (a_e^{Ga}) and tin (a_e^{Sn}) in the liquid eutectic at the onset of equilibrium solidification at eutectic temperature T_e (i.e., in the absence of supercooling) were calculated by the Shreder equation [12]

$$a_e^{\text{Ga}} = \exp \left[\frac{\Delta H_L^{\text{Ga}}}{R} \left(\frac{1}{T_L^{\text{Ga}}} - \frac{1}{T_e} \right) \right], \quad (5)$$

$$a_e^{\text{Sn}} = \exp \left[\frac{\Delta H_L^{\text{Sn}}}{R} \left(\frac{1}{T_L^{\text{Sn}}} - \frac{1}{T_e} \right) \right], \quad (6)$$

where ΔH_L^{Ga} and ΔH_L^{Sn} are the enthalpies of melting of gallium (5.59 kJ/mol) and tin (7.07 kJ/mol) [13] and T_L^{Ga} and T_L^{Sn} are the melting temperatures of gallium and tin, respectively.

The activity coefficients of gallium g_e^{Ga} and tin g_e^{Sn} under the same conditions were determined using the ratios of the activities to the component concentrations in the eutectic (X_e^{Ga} , X_e^{Sn}),

$$g_e^{\text{Ga}} = a_e^{\text{Ga}} / X_e^{\text{Ga}}, \quad g_e^{\text{Sn}} = a_e^{\text{Sn}} / X_e^{\text{Sn}}. \quad (7)$$

The table gives the activities and the coefficients of activities of the components in the eutectic. To estimate the activation energies of the components in the eutectic (see table) on the sides of gallium (W_e^{Ga}) and tin (W_e^{Sn}), the following expressions were used [14]:

$$W_e^{\text{Ga}} = \frac{\Delta H_L^{\text{Ga}} \left(1 - \frac{T_e}{T_L^{\text{Ga}}} \right) + RT_e \ln X_e^{\text{Ga}}}{(1 - X_e^{\text{Ga}})^2}, \quad (8)$$

$$W_e^{\text{Sn}} = \frac{\Delta H_L^{\text{Sn}} \left(1 - \frac{T_e}{T_L^{\text{Sn}}} \right) + RT_e \ln X_e^{\text{Sn}}}{(1 - X_e^{\text{Sn}})^2}. \quad (9)$$

Energies W_e^{Ga} and W_e^{Sn} were used to check activity coefficients g_e^{Ga} and g_e^{Sn} by the procedure described in [14], in particular, by the expressions

$$g_e^{\text{Ga}} = \exp \left[-(1 - X_e^{\text{Ga}})^2 W_e^{\text{Ga}} / RT_e \right], \quad (10)$$

$$g_e^{\text{Sn}} = \exp \left[-(1 - X_e^{\text{Sn}})^2 W_e^{\text{Sn}} / RT_e \right]. \quad (11)$$

The values of g_e^{Ga} and g_e^{Sn} obtained by Eqs. (10) and (11) (given in parentheses in the table) are close to those determined by Eq. (7).

An analysis of the aforementioned parameters for the supercooled metastable region at the onset of eutectic solidification is of particular interest. Let the activities in the eutectic at the metastability boundary be α_e^{Ga} and α_e^{Sn} , the activity coefficients be γ_e^{Ga} and γ_e^{Sn} , and the energies of mixing be ω_e^{Ga} and ω_e^{Sn} . As an

example, we used the maximum supercooling of eutectic alloy, $\Delta T_{\max}^E = 26$ K. To adapt Eqs. (5), (6), (8), and (9) to the calculation of the aforementioned parameters for the metastability boundary of the eutectic alloy, the metastability boundaries of gallium and tin should be taken into account. Since gallium, tin, and the Ga–8.5 mol % Sn eutectic alloy solidify under the same conditions in the present study, the corresponding boundary temperatures can be obtained as follows: $T_{\max}^{\text{Ga}} = \Delta T_L^{\text{Ga}} - \Delta T_{\max}^{\text{Ga}}$, $T_{\max}^{\text{Sn}} = \Delta T_L^{\text{Sn}} - \Delta T_{\max}^{\text{Sn}}$, and $T_{\max}^E = T_e - \Delta T_{\max}^E$, where $\Delta T_{\max}^{\text{Ga}} = 34$ K, $\Delta T_{\max}^{\text{Sn}} = 10$ K, and $\Delta T_{\max}^E = 26$ K.

In this case, the Shreder logarithm [15] “operates” and Eqs. (5), (6), (8), and (9) are reduced to the following form:

$$\alpha_e^{\text{Ga}} = \exp \left[\frac{\Delta H_L^{\text{Ga}}}{R} \left(\frac{1}{T_{\max}^{\text{Ga}}} - \frac{1}{T_{\max}^E} \right) \right],$$

$$\alpha_e^{\text{Sn}} = \exp \left[\frac{\Delta H_L^{\text{Sn}}}{R} \left(\frac{1}{T_{\max}^{\text{Sn}}} - \frac{1}{T_{\max}^E} \right) \right],$$

$$\omega_e^{\text{Ga}} = \exp \left[\frac{\Delta H_L^{\text{Ga}} \left(1 - \frac{T_{\max}^E}{T_{\max}^{\text{Ga}}} \right) + RT_{\max}^E \ln X_e^{\text{Ga}}}{(1 - X_e^{\text{Ga}})^2} \right],$$

$$\omega_e^{\text{Sn}} = \exp \left[\frac{\Delta H_L^{\text{Sn}} \left(1 - \frac{T_{\max}^E}{T_{\max}^{\text{Sn}}} \right) + RT_{\max}^E \ln X_e^{\text{Sn}}}{(1 - X_e^{\text{Sn}})^2} \right].$$

The table also gives the values of γ_e^{Ga} , γ_e^{Sn} , ω_e^{Ga} , and ω_e^{Sn} . A comparison of these values shows that the a_e^{Ga} and α_e^{Ga} activities of gallium in the eutectic are higher than the a_e^{Sn} and α_e^{Sn} activities of tin under equilibrium conditions (at $\Delta T_{\max}^E = 0$) and for the metastable region (at $\Delta T_{\max}^E = 26$ K). This can be explained by the fact that the eutectic gallium concentration (91.5 mol %) is higher than the tin concentration and that the majority of the solid phase in the eutectic melt at the moment of solidification (ES, NES) is occupied by the α gallium solid solution, the tin solubility in which is only 0.226 mol %.

As the same time, it is seen that the activity of gallium α_e^{Ga} at $\Delta T_{\max}^E = 26$ K is higher than the a_e^{Ga} activity at $\Delta T_{\max}^E = 0$. For tin, inversely, the activities for the supercooled region are lower than those at $\Delta T_{\max}^E = 0$ ($a_e^{\text{Sn}} > \alpha_e^{\text{Sn}}$). In passing into the metastable region, the activity of gallium in the eutectic is likely to increase during incubation period τ_i , suppressing the activity of

tin. The more abrupt change of the activation energy of tin ($\omega_e^{\text{Sn}}/W_e^{\text{Sn}} \approx 2.29$) as compared to that of the activation energy of gallium ($\omega_e^{\text{Ga}}/W_e^{\text{Ga}} \approx 1.64$) in the eutectic can be related to the fact that tin is less active when crystals form in the eutectic. This can be indicated by the similarity of the solidification curves of gallium [8] and the eutectic Ga–91.5 mol % Sn alloy and the explosive solidification of the alloy.

CONCLUSIONS

- (1) The effect of overheating of the Ga–8.5 mol % Sn eutectic melt on the presolidification supercooling was studied by cyclic thermal analysis. It was found that the dependence of the supercooling on the overheating exhibits monotonic ascending behavior. The maximum supercooling is 26 K.
- (2) The fraction of the solid phase (η) at the onset of nonequilibrium solidification was calculated; at an supercooling of $\Delta T_e^- = 4, 13$, and 26 K, it is 0.025, 0.07, and 0.14, respectively.
- (3) The Avrami parameter ($n = 1.25$) and the nucleation constant ($Z \approx 7.4 \times 10^{-2}$) were calculated using the Avrami–Kolmogorov equation.
- (4) The activities of gallium and tin in the liquid eutectic at the onset of equilibrium and nonequilibrium explosive solidification were calculated. It was found that the activity of gallium is higher than that of tin under all conditions.

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