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INVESTIGATION OF MASS TRANSFER IN THE COMPLEX SYSTEM Te–Tl BY THE CONTACT-MELTING METHOD

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An investigation of the kinetics of contact melting of the complex system Te–Tl under unsteady diffusion conditions is made. The growth of the contact interlayer obeys a parabolic law. The interdiffusion coefficient $\tilde{D}$ *is calculated in the temperature range 260–300°C. It has been found that* $\tilde{D}$ *virtually does not change within the temperature range 260–280°C. The effect of decrease in the temperature of contact melting relative to the equilibrium eutectic is established. A relationship between the superheating of a melt of the stable eutectic and the magnitude of its supercooling is found.*

The Te–Tl system has a complex phase diagram and is characterized by the presence of several chemical compounds [1]. Tellurium and Tl_2Te_3 form a eutectic at 29 at.% Tl and 224 ± 2°C. Peritectic formation of Tl_2Te_3 can easily be suppressed before the beginning of the reaction; here Te forms a metastable eutectic with TlTe at 203°C and ~31 at.% Tl. The compound TlTe is formed as a result of a peritectic reaction at 300°C [1].

An abnormal temperature dependence of the diffusion coefficients has been established for the Te–Tl system. In an alloy containing 42.7 at.% Tl the interdiffusion coefficient decreases with increase in the temperature, while in an alloy with 33.8 at.% Tl, it remains unchanged within the temperature range 300–400°C [2]. There is information that the temperature coefficient of surface tension of Te–Tl alloys can acquire, depending on the composition, both positive and negative values [3]; the presence of chemical compounds has no effect on the isotherms of surface tension in the liquid state. In the opinion of Alchagirov et al. [3] this is associated with possible dissociation of the indicated compounds.

Valuable information on the processes occurring in systems with chemical interaction of the components is provided by investigations of contact melting in these systems. Contact melting represents formation and growth of a liquid phase during contact of unlike crystals. The process of contact melting proceeds in different classes of substances that have a phase diagram with a minimum point on the liquidus curve.

In systems with chemical interaction of the components, the phenomenon called the ΔT (delta T) effect occurs. It consists in formation of a liquid during contact of unlike crystals at a temperature lower than the melting point of the lowest eutectic [4, 5]. In the opinion of a number of authors [5, 6], this effect is observed in the case of suppression of compound formation when the crystals are in contact.

In investigations, we used metals of the following grades: thallium – T1-00, tellurium – T-V3 (no less than 99.99% of the basic component). The samples were produced by drawing from a melt. Te–Tl alloys of eutectic composition (29 and 31 at.% Tl) were prepared by melting the components in silica crucibles under the protection of a layer of PFMS-2.5 silicone oil. Experiments on contact melting were carried out according to the procedure of [7, 8].

Figure 1 presents dependences of the squared extent of contact interlayers δ^2 of the Te–Tl system versus the time τ under unsteady diffusion conditions at experimental temperatures of 290 and 300°C. As is

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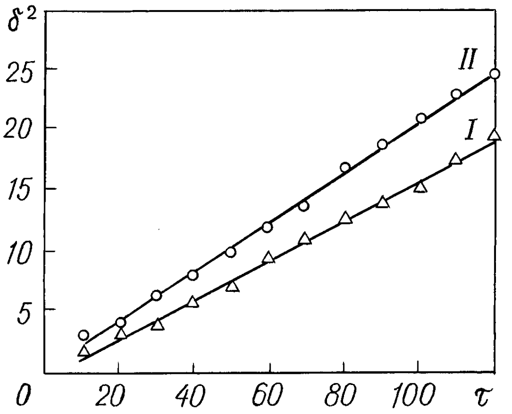

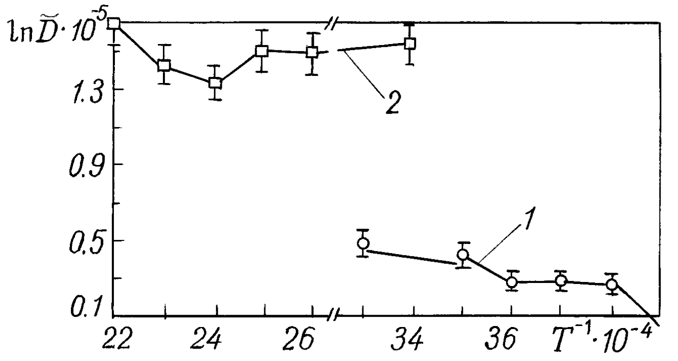

Fig. 1. Plots of $\delta^2(\tau)$ in the Te–Tl system for temperatures of 290 (I) and 300°C (II). δ^2, mm^2; τ, min.

Fig. 2. Plots of $\ln\tilde{D} = f(1/T)$ for the Te–Tl system. $\ln\tilde{D}$, cm^2/sec; T^{-1}, K^{-1}.

TABLE 1. Data for Determination of T_E by Formula (2)

System	C_1, at.%	C_2, at.%	T_1, K	T_2, K	L_1, J/(g·mole)	L_2, J/(g·mole)	Q_{12}, J/(g·mole)	Z_m	R, J/(g·mole)	T_E, K
Te–Tl	0.71	0.29	723	576	17430.6	4270.54	17940	5	8.31	462

seen from the figure, the change in the extent of the diffusion zone with time obeys the parabolic law $\delta = \alpha\sqrt{\tau}$.

From the data on the kinetics of contact melting carried out under unsteady diffusion conditions the interdiffusion coefficient $\tilde{D}$ is found from a formula obtained in [7]:

$$\tilde{D} = \frac{\delta^2}{2\tau}\frac{C_1(1-C_2)}{(C_2-C_1)(C_1-C_2+1)}. \tag{1}$$

Calculation by (1) was carried out under the assumption of nondependence of the interdiffusion coefficient on the concentration.

Figure 2 gives the calculated dependence $\ln\tilde{D} = f(1/T)$ (curve 1) and data from [2] (curve 2). From the figure it follows that the interdiffusion coefficient remains practically constant within the temperature interval 260–280°C. A similar temperature dependence of $\tilde{D}$ for an alloy with 33.8 at.% Tl in the temperature range 300–400°C was obtained in [2].

Using the formula [5]

$$\exp\left(\lambda_1 - \frac{Q_{12}}{2RT_E}a\Phi_{1E}^{\mathrm{liq}}\right) + \exp\left(\lambda_2 - \frac{Q_{12}}{2RT_E}a\Phi_{2E}^{\mathrm{liq}}\right) = 1 \tag{2}$$

the decrease in the temperature of contact melting T_E relative to the stable eutectic was calculated. Calculation by (2) was carried out on a computer using the data from Table 1.

As follows from the results obtained, the calculated decrease in the temperature of contact melting relative the stable eutectic is 34 K.

According to [1], the difference in the melting points of the stable and metastable eutectics is 21 ± 2 K. The experimental value of the temperature at which we recorded the "setting" of the samples was 489

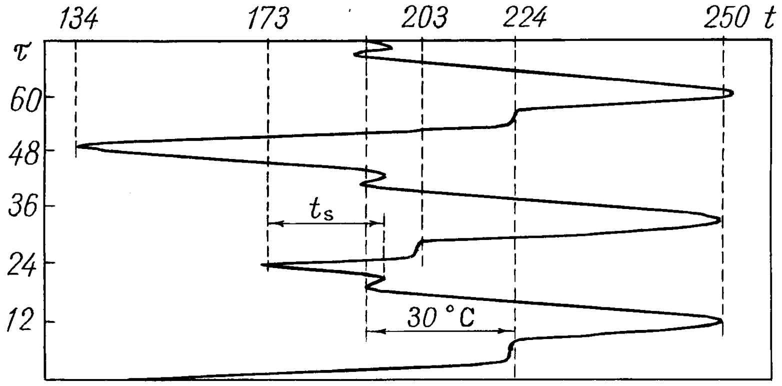

Fig. 3. Melting and crystallization thermograms for the alloy with 29 at.% Tl. t, ^oC.

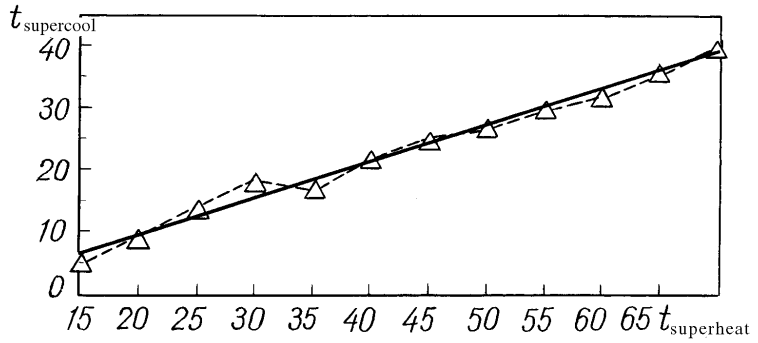

Fig. 4. Supercooling versus temperature of superheating for the alloy with 29 at.% Tl.

K (ΔT = 8 K). A metallographic analysis showed the islet character of the zone of "setting" of the samples; its structure represented the structure of a hardened liquid: dendrites and crystallization blocks.

The disagreement between the theoretical and experimental values of ΔT is associated, apparently, with certain approximations used in [5] in deriving the calculational formula (2) and with the difficulty of finding the small amount of liquid phase formed in contact of the Te and Tl samples.

The liquid phase occurring in complex systems at a temperature lower than that of the equilibrium eutectic crystallizes, as a rule, immediately, which is indicative of its supercooled state.

Thus, one necessary condition for the ΔT effect to manifest itself is, in our opinion, the capacity of alloys of the corresponding concentrations for being supercooled. To check this statement, we carried out thermographic studies of alloys of the Te–Tl system corresponding to the equilibrium (29 at.% Tl) and metastable (31 at.% Tl) eutectics and also a differential thermal analysis (DTA) of the compounds Tl_2Te_3 and TlTe.

The thermal analysis was carried out in a special tubular electric furnace with the use of a KSP-4 automatic potentiometer and a glass-enclosed Chromel-Copel thermocouple that was immersed directly in the melt in a Pyrex test tube. The error in determining the temperature was $\pm 3^oC$. The thermal analysis of the compounds was carried out using a Chromel-Copel differential thermocouple whose cold junction was placed in a Dewar filled with thawing ice. The heating rate of the alloys was varied from 5 to 20 deg/min; the cooling was carried out either in the furnace at a constant rate of $\sim 10^oC$/min or in air.

Figure 3 presents melting and crystallization thermograms of the 29 at.% Tl alloy. As is seen from the figure, in some cases the investigated alloy begins to melt at 224 ± 3^oC, and in other cases, at 203 ± 3^oC. According to [1], this is explained, in the first case, by the presence of Tl_2Te_3, and in the second case (sup-

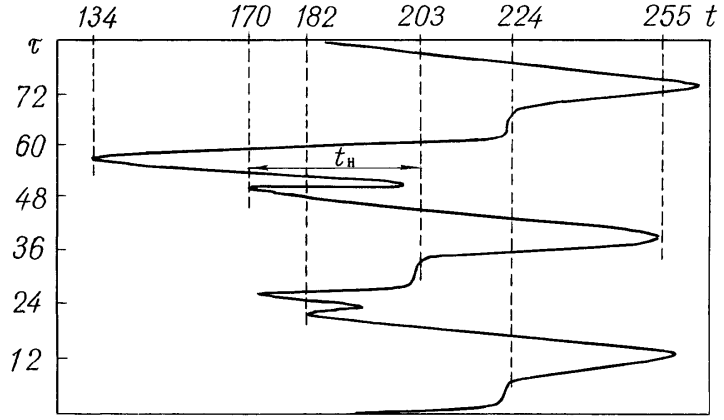

Fig. 5. Thermogram of spontaneous crystallization for the alloy with 29 at.% Tl.

pression of the peritectic reaction of formation of the indicated compound), by formation of the metastable Te–TlTe eutectic.

It is not ruled out that the small temperature-time interval t_s of cooling of the solid alloy is insufficient for formation of the compound Tl_2Te_3.

On the other hand, it is possible that crystallization of the supercooled melt, which proceeds at a high rate, leads to displacement of the liquidus and solidus curves outside the eutectic horizontal [9]. Then none of the phases composing the eutectic or the peritectic is formed or participates in the interaction [10].

In crystallization of the stable Te–Tl_2Te_3 eutectic, one can observe supercooling of the melt: ~40°C.

A certain relationship exists between the temperature of superheating above the melting point of the alloy and the value of the supercooling.

Figure 4 depicts the relation between the temperature of superheating above the melting point of the 29 at.% Tl alloy and the value of the supercooling.

In our opinion, the dependence of the value of the supercooling on the superheating temperature can be explained using the ideas suggested in [10]. One conclusion of this work is the possibility of the existence of two structural states in the melt. In heating of the melt, the "low-temperature" state can pass abruptly to a "high-temperature" state capable of substantial supercooling. In this case, crystallization of the melt can proceed from the "low-temperature" state or from the "high-temperature" state.

In superheating of the melt by 50–55°C relative to the melting point of the metastable eutectic (the "high-temperature" state), the following special feature is observed: crystallization in air proceeds spontaneously over the entire volume of the melt and is accompanied by vigorous heat release (the section t_{low}); as a result, the melt temperature increases again to the melting point of the metastable eutectic (Fig. 5).

The reason for the spontaneous crystallization is, most probably, heterogeneous formation of the compounds Tl_2Te_3 and (or) TlTe in the supercooled melt. Their formation, as is seen from the DTA curves, is accompanied by several exothermic effects at 290, 240, and 190°C; melting is accompanied by endothermic effects at 238 and 300° (Fig. 6).

A comparison with the phase diagram of the Tl–Te system shows that at 290 ± 3°C the compound TlTe begins to crystallize, at 240 ± 3°C crystals of Tl_2Te_3 fall out, and the peak at 190 ± 3°C corresponds to cessation of crystallization.

For the alloy corresponding to the composition of the metastable eutectic (31 at.% Tl), no clear dependence of the value of the supercooling on the superheating temperature was established.

For different temperatures of superheating (from 15 to 55°C) the value of the superheating was 3 to 57°C.

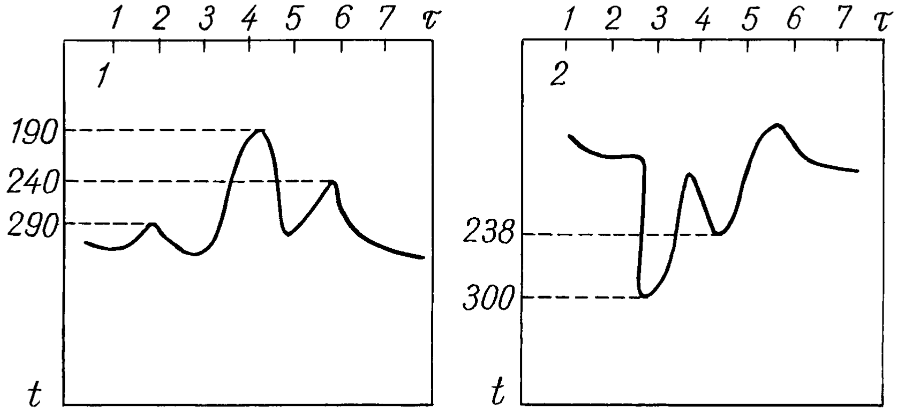

Fig. 6. DTA curves for the compounds Tl_2Te_3 (1) and TlTe (2).

Thus, the results obtained allow us to assume that the processes proceeding in the Te–Tl system within the temperature range 200–300°C are characterized by rearrangement of the structure.

According to [11], the structure of tellurium represents zigzag spiral chains of atoms arranged one above the other. The rows of atoms combine to form a spiral chain. The bond between tellurium atoms in the chains is covalent, the interaction between the chains occurs by the action of weak van der Waals forces, which explains the easy spallation of Te crystals in planes parallel to the chain axes.

In the melting of tellurium, not only weak van der Waals bonds but also some covalent bonds are broken. In melting, the density of tellurium decreases abruptly by approximately 6%, which is indicative of loosening of the structure as a result of an increase not only in the interatomic distances in a chain but also in the distances between the atomic chains. In the liquid state the density of tellurium decreases with increase in the temperature. In the interval 453–500°C, the density of tellurium increases, which is associated with compaction of the chains.

In the investigated temperature range (200–300°C), the special features of structurization in liquid and solid alloys that are analyzed in [12] are apparently manifested, in particular, the possibility of suppressing the formation of individual phase components of the alloy by temporal heat treatment.

It is not ruled out that in the melting of Te–Tl alloys the short-range order is not destroyed completely, and this inevitably has an effect on the crystallization temperature of the melt. This can be responsible for the small supercooling of the melt with small superheatings above the melting point. Moreover, the special features observed in the Te–Tl system can be attributable to the complex structure of its components that has been discussed above.

Thus, the suggested idea that a necessary condition for manifestation of the ΔT effect is the capacity of the melt of the stable (metastable) eutectic for being supercooled has been verified experimentally by the method of thermal analysis.

NOTATION

δ, extent of the diffusion zone; α, constant of growth, coefficient of proportionality between δ and $\sqrt{\tau}$; τ, time of growth of the diffusion zone; $\tilde{D}$, interdiffusion coefficient; C_1 and C_2, liquidus concentrations determined from the phase diagram; $\lambda_i = (\mu_i^{(0)(s)} - \mu_i^{(0)(liq)})/RT_E$, $i = 1, 2$; $\mu_i^{(0)(s)}$ and $\mu_i^{(0)(liq)}$, chemical potentials of the pure i-th component in the solid and liquid states; R, universal gas constant; T_E, temperature of the eutectic; Q_{12}, characteristic temperature of the eutectic; $a = \frac{1}{4} \exp\left(\frac{Q_{12}}{RT_E Z_m}\right)$; Z_m, mean coordination number of the eutectic alloy; $\Phi_i = (1 + 4C_iC_j \pm c/a)^2 + \frac{2C_j \pm i(1 - 2C_i)}{a(1 + 4C_iC_j \pm i/a)}$; t, crystallization temperature of the alloy, $^{\circ}$C; t_s, small temperature interval by which the solid-state alloy is cooled, $^{\circ}$C; t_{low}, section of the low-temperature state; $t_{\text{supercool}}$, supercooling temperature; $t_{\text{superheat}}$, superheating temperature; t_{crys}, crystallization temperature; T_1 and T_2, melting points of the pure components; C_i and C_j, concentrations of the components in the eutectic.

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