The thermal physical properties and structure of In-In₂Bi eutectic at melting-crystallization process

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Abstract

The physical properties of In-In2Bi liquid eutectic alloy as well as structure has been studied at different temperature. Structure data are used for calculation of configuration entropy. The change of structure upon melting is analyzed in comparison with change chemical bonding. The data on acoustic emission studies at meting and crystallization processes are analyzed too.

Key words: molten In-Bi alloys, short range order structure, viscosity, melting.

I. Introduction

Alloys on the base of Bi are widely used in engineering on due to their low melting temperatures and high corrosive resistivity in liquid state. In recent years the interest to these alloys is also motivated by their promising use as Pb – free solders. Beside the above mentioned peculiarities Bi reveals some other useful unique properties such as, first of all, the decreasing of their atomic volume and drastic change of magnetic susceptibility upon melting.

Bismuth is a semimetal; that's why its crystalline structure is formed via both metallic and covalent bonding. During melting the covalent bonds break but this process is completed only upon overheating above melting temperature which is confirmed by the presence of hysteresis behavior of main properties.

We have obtained the unrepeating values of thermo-power (α) for Bi at melting and crystallization (Fig. 1).

2. Thermo-power and entropy

Commonly the Mot formula is used in order to calculate the thermo-power for liquid metals:

$$\alpha = \frac{\pi^2}{3} \cdot \frac{k_B^2 \cdot T}{e} \left[\frac{\partial \ln \sigma}{\partial E} \right]_{E=E_F} \tag{1}$$

where σ – electroconductivity; E_F – Fermi energy; k_B – Boltzmans constant.

Therefore the charge of transfer value is in power one in this formula. Consequently the absolute thermo-power has its own sign as well as Hall constant. It can be written:

$$\frac{\partial \ln \sigma}{\partial E} = \frac{\partial \ln \lambda}{\partial E} + \frac{\partial \ln G}{\partial E} \tag{2}$$

This formula allows us to conclude that σ(E) function depends both on free path length and Fermi surface square G. Be-

sides, the first term in (2) is positive always, whereas the second one can be negative depending on the shape of Fermi surface.

Let us introduce the α_F parameter in the following way:

$$\alpha = \alpha_F \cdot E_F \cdot \left[\frac{\partial \ln \sigma}{\partial E} \right]_{E=E_F} \tag{3}$$

Free electron model [2] yields:

$$\alpha_F = -2,45 \cdot 10^{-2} \cdot \frac{T}{E_F} \tag{4}$$

The approximation for weak bounded electrons and assumption that Fermi surface is a sphere, electroconductivity equals:

$$\sigma = A \cdot E_F \tag{5}$$

Coefficient A can be determined from experimental values of electroconductivity σ_{exp} and Fermi energy E_F, calculated from experimental values of Hall constant R:

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 N \right)^{2/3} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{R \cdot e} \right)^{2/3} \tag{6}$$

Therefore coefficient A calculated in such a way can be used in order to obtain $\sigma(E)$ dependence on arbitrary Fermi level. Having already obtained $\ln \sigma = f(E)$ dependence one can obtain $\frac{\partial \ln \sigma}{\partial E}$ near real value of Fermi energy using the graphic derivative method. We can use these results for the estimation of theoretical values of thermo-power according to (3), (4) equations.

Obviously, the temperature dependence of thermo-power calculated according to above described procedure represents $\alpha(T)$ values for the case of disordered metallic structure formed in molten bismuth upon complete degradation of its covalent bonds. Its contribution to total chemical bonding is still significant within some temperature range after melting. It should be noted that calculated $\alpha(T)$ dependence is significantly different from experimental one even just upon melting, but approaches it with heating and becomes the same upon 400K overheating above melting temperature. This fact confirms the existence of significant temperature range of liquid Bi structure transformation.

Hence, we explain the hysteresys in $\alpha(T)$ experimental dependence by complete topological disordering and metallization of chemical bonding occurring within some temperature range upon melting. Consequently the absolute values of thermo-power reach the level, predicted by weakly bonded electrons theory.

It is important that these values of persist at following cooling of homogeneons melt as low as deep overcooling, when the melt rapidly returns to crystalline state with covalent-metallic bonding.

The presence of significant temperature range in transition to pure metallic structure can also be illustrated by temperature dependence of configuration part of entropy (fig.1) calculated from pair correlation function g(r) according to the formula:

$$S_{конф.} = -2 \cdot \pi \cdot R \cdot \rho_0 \cdot \int_0^\infty g(r) \cdot \ln g(r) \cdot r^2 \cdot dr \tag{7}$$

where ρ_0 – mean atomic density; R – gas constant; g(r) – pair correlation function.

The pair correlation function for liquid Bi is calculated from experimental structure factors obtained by means of x-ray diffraction method in [3].
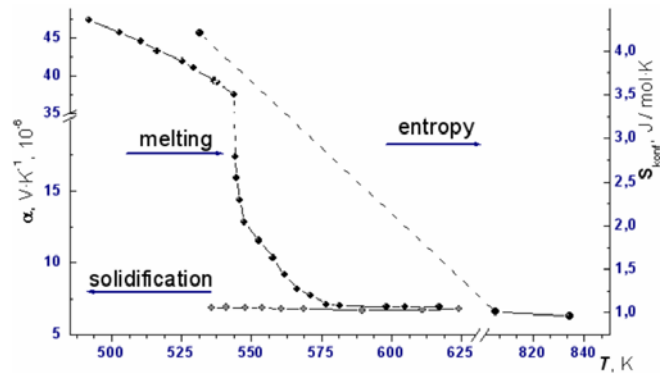

Fig. 1 — Temperature dependence of thermo-power (α) and configuration entropy (S_{konf} for Bi at melting and crystallization.

It follows from dependence represented in fig.1 $S_{konf}^{Bi} = f(T)$ that complete topological disordered state in structure appears at $T \leq 700$ K. For more accurate estimation of disordering range the diffraction data with small temperature step are needed.

It is clear that pecularities of precrystallization in structural-thermodynamic state will also take place in alloys with Bi, which fact should be taken into account in such practical processes as casting, soldering, welding as well as in using molten alloys as coolants in nuclear power stations. Bi-based molten alloys will reveal nonequilibrium structure within some temperature range; it should be taken into account when controlling melting and solidification processes.

The structural-thermodynamic state is especially important in metrology, where even such small deviation of phase transition temperature as 0,01 K is unacceptible [4].

Now we consider the results for complex In-In$_2$Bi eutectic alloy. For studying of melting and crystallization processes the methods of x-ray diffraction, viscosity measurements, differential-thermal analysis, calorymetry and acoustic emission were used.

3. Melt structure and viscosity

The results on x-ray diffraction studies of In-In$_2$Bi eutectic melt at temperatures 363K; 433K and 473K are shown in fig.2.

In this figure the intensities corresponding to diffraction patterns for crystalline In and Bi at room temperature are also shown.

Experimental intensity curves for In-In$_2$Bi molten eutectic alloy show some peculiarities. The principal peak positions are significantly shifted to lower s-values in comparasion with ones for pure liquid In and Bi. Another feature is the existence of the shoulder on the right hand side of principal maximum. This shoulder persists at higher temperatures available in our investigation. Some smearing of it is observed at T=473K. The similar maximum is also the characteristic of structure factor for liquid Bi but it is preserved up to very high temperatures (~ 1300K). Tak-

ing into account such behavior of the shoulder one can suppose that the existence of self-associated Bi groups in the structure of molten eutectic alloy is impossible.
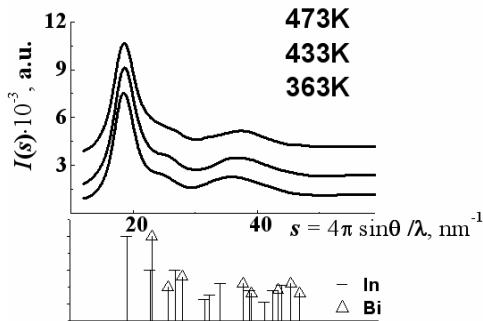

Fig.2 — The x-ray scattered intensity curves for molten In-In$_2$Bi eutectic alloy at 363K; 433K and 473K and diffraction pattern reflexes at room temperature.

Detailed analysis of intensities curves and pair correlation functions calculated from them by means of Fourier transformation permitted us to conclude that liquid eutectic alloy consists of chemically ordered clusters (associates) of In$_2$Bi steichiometry, randomly distributed in In-matrix.

Interatomic distance in In$_2$Bi clusters is less than one in assumption of random atomic distribution, since there is strong covalent bonding between In and Bi atoms. The total structure in this case can be considered in the frame of "cluster jelly" model (disordered matrix + clusters) where the structural defects are ejected from cluster volume in matrix and the correlation between clusters distribution can be neglected. Thus, due to a large fraction of defects near the clusters boundaries and less density of packing for clusters with stronger bonding between atoms in them, that corresponds to larger surface energy, the mean interatomic distance is suggested to be longer than in random atomic solution.

The complicated structure, which is considered as superposition of densely packed clusters with chemical ordering, the clusters, the structure of which correspond to α-phase (In(Bi) – solution) and chemically disordered matrix becomes significantly simpler with heating. Unfortunately, the diffraction methods cannot provide answers to whether the disordering of associates is a gradual process (diffusive) or an activated one. It is the viscosity measurement that can provide the answer.

The viscosity dependence on temperature $\nu(T)$ within wide temperature range and calculated values of $\ln\nu = f(1/T)$ function are shown in fig.3.

Fig.2 — The x-ray scattered intensity curves for molten In-In$_2$Bi eutectic alloy at 363K; 433K and 473K and diffraction pattern reflexes at room temperature.

As it can be seen there is anomaly in both temperature dependences at 600÷610K region. The observed change in temperature dependence behavior is supposed to be caused by transition of linear dependence in $\nu(T)$ (it occurs at high temperatures) to exponential one, which is commonly pronounced at precrystallization temperatures. Representing the activation energy of viscous flow according to Frenkel and Ering equations as an angle of slope in logarithmic dependence, we can assert that in temperature

region 600÷610K the In$_2$Bi clusters are broken. Hence the process of structure change reveals the threshold behavior.
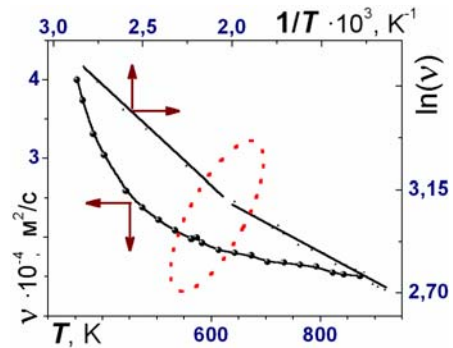

Fig.3 — Viscosity $\nu(T)$ and $\ln\nu = f(1/T)$ function for In-In$_2$Bi eutectic melt.

It is known that viscosity value can be used in order to estimate the degree of short range order:

$$a_1 = 1 - \frac{\eta_1\eta_2}{\eta\left(x_1\eta_2 - \eta_1 x_2\right)} \tag{8}$$

The short range order parameter α_1 calculated according to this formula using the data on dynamical viscosity coefficients for eutectic melt η and for constituents η_1, η_2 has negative value at low temperatures undergoes inversion at and takes time positive values at higher temperatures.

This fact is also confirmed by the transition of microinhomogeneous structure to random atomic distribution.

4. Crystallization: differential thermal analysis (DTA) and acoustic emission (AE)

The differential thermograms for In-In$_2$Bi eutectic alloy at melting and crystallization processes (before heated up to T_{melting} + 30 K) are shown in fig.4.

The experiment was carried out at the same heating cooling rate. The next three features should be taken into account:

The square under crystallization maximum is 15 – 17 % larger than the one corresponding to melting process. Accounting to the same heating and cooling rate such significant difference can be attributed to incompleteness of structure transformation processes at melting temperature and their continuation within some temperature interval upon transition to liquid state. These data confirm the above described results on x-ray diffraction investigation.

Another feature is the presence of inflection point behind the crystallization peak. Taking into account its small size one should be careful interpreting it. However the results of more precissive calorymetry investigation [4] near the phase transition point also reveal the additional thermal effect, confirming the existence of incongruent In$_2$Bi intermetallic compound and its complex step by step formation according to peritectic reaction.

The third feature of cooling thermogram is the significantly high second maximum at temperature about 33 °C, which may be

the attributed to phase recrystallization process, not indicated in available phase giagrams.
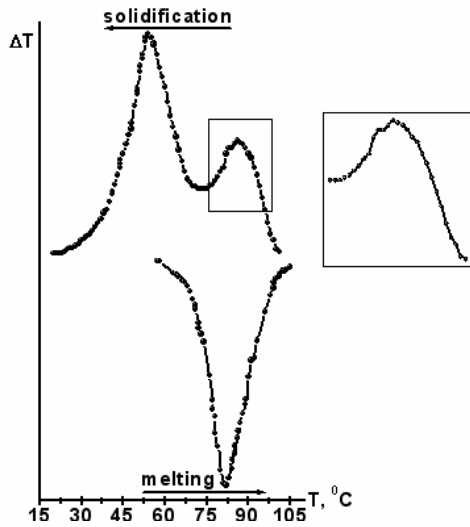

Fig.4 — Differential thermograms of melting-crystallization processes for In-In$_2$Bi eutectic alloy.

The results of studying crystallization process by means of acoustic emission are shown in fig.5, 6. The acoustic radiation was generated during crystallization process of In-In$_2$Bi eutectic melt. Parameters of AE are also shown in fig.4 in order to compare them with the differential thermogram in the same time base.

The dynamics of crystallization process is revealed by the parameters represented in fig.5, where E_t — time dependence of radiated sound energy (measure of radiated energy activity); sE_t — total accumulated energy is released in some frequency band during some selected time interval.
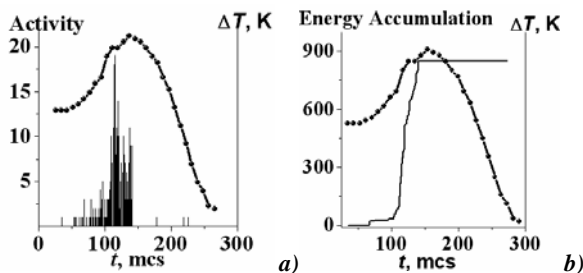

Fig.5 — Dependence of acoustic emission parameters on time: a) activity of released energy; b) accumulation of energy.

Accumulated sound energy time dependence is nonlinear. During the first stage ($\approx$100 c) the low level of random interaction between crystallization centers have a contact over all volume and as result the sound energy rapidly increases until to complete crystallization. It should be noted that accumulation of sound energy continues still upon initial crystallization is completed. One can assume that it is connected with recrystallization and stoichiometry change of intermetallic at peritectic reaction.

The degree of criticality (completeness) of the process can be estimated from fig.6 where the amplitudes of signals (A_t) and "catastrophic coefficients" of process (K_p) are shown.
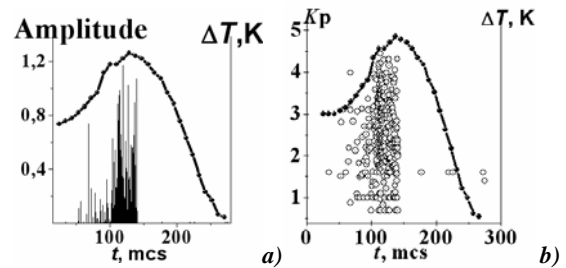

Fig.6 — Dependence of acoustic emission parameters on time: a) signal amplitude; b) catastrophicity parameter.

Functional dependence $A_t = f(\tau)$ (fig. 6 a) confirms the fact that developments of large intensity (high amplitude) are not completed with completing of phase transition, but continue corresponding to submaximum in thermogram, that can also be interpreted as phase recrystallization.

K_p parameter is connected with the rate of AE generating processes. This parameter is a function of energy density change, corresponding to recorded AE – signals. Value of K_p is proportional to acceleration of material rebuilding (level of acoustic modification). It is established empirically that such rebuilding becomes irreversible when $K_p \geq 3,0$. It follows from fig.6b that such irreversibility can be reached after $\tau \rightarrow 100$ s. The value of K_p is also higher than critical one behind the maximum in thermogram that is caused by above mentioned recrystallization of formed intermetallic.

Conclusions

Thus the complex analysis of the results of thermoelectric, x-ray diffraction, viscosity, thermography and acoustic emission studies using the above considered models allows us to obtain not only qualitative, but also quantitative data on the structure transformation, needed especially for developing the technology for optimal control over crystallization processes.

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