



Physical and technological preconditions of melting-crystallisation temperature stabilisation

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Received 12.03.2008; published in revised form 01.07.2008

ABSTRACT

Purpose: The precise temperature measurements need the using of temperature reference points - „temperature fixpoints” (TFP). The increase of measuring temperature interval and other reasons require of new TFP with high stability in different working conditions. On that reason the studying of liquid metals and metallic eutectic alloys has been carried out in this work.

Design/methodology/approach: For experimental studies the physical properties measurements were used.

Findings: Non-reproducibility of temperature fixpoints exist due to some reasons: no accounting the structural - thermodynamic state of melt; mass-heat processes are not enough taken into account. It is fixed, that the temperature fluctuations (and non-stability of crystallization plateau) are of two types: small fluctuations (up to (1-2) mK) are caused by phases (stages) of crystallization process; major fluctuations (at us: $\pm 0,2K$) crystallizations are caused convectional streams at the front. Fluctuations can be essentially reduced by approach to requirements of thermodynamic balance, but their complete elimination - is problematic.

Research limitations/implications: The main parameters obtained from them are analysed. It is shown that melting-crystallization phase transition is influenced by structural state of melt and cooling condition.

Practical implications: The results obtained here can be used in analysis of errors at high-precision temperature measurements and constructing of new temperature measuring and holding systems of high stability.

Originality/value: The results of this study can be useful for researches in field of metrology, material science and physics of metals.

Keywords: Metallic alloys; Heat treatment; Melting; Structure Modification; Thermopower; Temperature fix-points

MATERIALS

1. Introduction

It is known that most precise and reliable method of temperature stability checking of temperature sensors is the periodical control in respect to the temperature reference points (temperature fix-points — TFP), that mainly are determined as melting-crystallization phase transition temperatures.

At same time it should be noted here that existing international temperature scale (ITS-90) consists the TFP with no regular distributions. Besides, the approximations equations unable to estimate the thermodynamic temperature with high accuracy what is required in many technological processes of various industrial areas.

Above $T=234$ K the TFP of ITS-90 are the crystallization temperatures of pure Hg, In, Sn, Zn, Al, Ag, Au, Cu and melting temperature of Ga at conditions close thermodynamic equilibrium between liquid and crystalline phase. Unfortunately this demand is declarative only, and is not established by technical conditions. Besides the reproduced of melting temperature suggested by ITS-90 equals: ± 0.1 (In), ± 0.1 (Sn), ± 0.2 (Zn), ± 1.0 (Cu), ± 5.0 (Ag) mK. But very soon upon ITS-90 introducing in practical use the results on comparing of TFP for tin and zinc reveal the discrepancy ≥ 1.5 and ≥ 2.4 mK respectively [1]. In result the discrepancy in reference point values is ≥ 1.5 mK for tin and ≥ 2.4 mK for zinc. That is by one degree higher than regimented one. The later fundamental metrologic investigations [2] confirm the discrepancies between manifested by ITS-90 scale and real accuracies. Besides the crystallization temperatures were no reproduced in the same way.

At present time the temperature reproduce accuracy by ITS-90 not satisfy the requirements of modern science and industry. Just on that reason the improvement of methods for stabilization of temperature (reference-/fix-) point (TRP) is of high priority task, whose solutions optimal and consistent realization of melting-crystallization phase transformation in order to create and certify the new more improved ITS.

Certainly that at first the question arises: which direction of phase transitions should be selected the have the better temperature reproducibility. Obviously the melted should be selected because the crystallization process can be considered as a sum of few process, that melting should be selected because the crystallization is accompanied by overcooling. Nevertheless ITS-90 in fact for over pure metals recommends using the crystallization process. This recommendation is motivated: a) crystallization process is very close to thermodynamics equilibrium one at slow cooling before solidification; b) heterogeneous crystallization is promoted by thermal factor only; c) the structure formation occurs at very slow radial heat transfer to outside wall of cylinder reference cell.

These recommendations are rational but unfortunately they are qualitative only and consequently inconclusive. Particularly: a) initial structural state of some definite melt does not account; b) the velocity of crystallization zone moving does not regiment; c) heat and mass transfer (especially near crystallization front) is ignored.

Not we attempt to analyze these aspects on the base of our results and some literature ones.

2. The structure transformations an entropy of melt

The active random atomic motion is the reason that melt exists in state far from stable static arrangement of atoms, but most probable structural distribution can be determined. Quantative characteristic of such distribution is the structure factor, which is commonly derived from experiments of diffraction of X-ray or neutron radiation.

The structure factors describe the atomic distribution in s -space and allow obtaining some structure parameters. It shows what is the difference between atomic distribution in some definite system of atom from one where atoms where randomly distributed (like to gases).

In order to describe the structure in real space the pair correlation function $g(r)$ was calculated. Maxima positions in $g(r)$ function are considered as the most probable interatomic distances. This function allows also estimating the number of neighbours Z and correlation radius R_{cor} . Most important structure parameters obtained from diffraction data for some liquid metals and compared with structure parameters for crystalline one.

Analysis of these structure parameters shows the similarity of liquid metals structure. This fact lies in the base of hard sphere model, which enable to the structure of simple liquid metals using two parameters only – hard sphere diameter and packing density. Different values of these parameters are responsible for the structure factors change from one metal to another of with temperature change. But it attempt to final the influence of structure changes before crystallization of melting should be accounted. Especially it is important in case of metrology.

Now we shall analyze in more detail features the structure of such liquid metals as In, Ga, Sn, Al and Bi as well as their physical properties. These elements are typical representatives of different kind liquid metals and are more attractive for using them as TRP elements. They form eutectic alloys which also can be used in temperature measurement systems. From mentioned above group of metals the crystalline structure of In and Al is based on dense atomic packing as in typical simple metals. Tin as premelting temperatures reveal tetragonal structure due to some part of covalent bonds. Gallium and bismuth are typical semimetals, whose interatomic bonds also reveal the some part of covalence.

Such structure is differences should be displayed in mechanism of melting. It is known that Bi and Ga decrease their atomic volume. Therefore, these elements reveal the formation of more densed short range order ($Z_L > Z_S$), whereas another elements (In, Sn, Al, Cu, Ag, Au) show the opposite behavior ($Z_L < Z_S$). With heating the number of neighbors Z for typical metals after melting decreases, whereas it changes insignificantly in case liquid semimetals.

There are some characteristic features in profile of structure factors. Particularly the principal peaks for In, Sn, Al, Cu, Ag, Au are symmetric and second to first peak positions ratio equals 1,85. Both two features are characteristic for other liquid metals with dense packed atomic distribution but the temperature dependences of structure factors for each element are different.

Te structure factors of tin and especially Ga and Bi show the significant deviation from ones for liquid metal with dense packed atomic distribution. Principal peak is asymmetric with shoulder on right hand side.

This shoulder persists with temperature and disappears upon significant overheating.

Another structural parameter – correlation radius, determining as minimum distances from initial atom where the correlation in

interatomic distribution disappears, was determined from pair correlation function. The value of this parameter for liquid Bi and Ga near the melting point temperature is within the 1.8-2.0 nm. For molten dense packed metals R_{conf} is significantly less (1.2-1.5) nm, initiating the existence of less inhomogeneous in atomic distributions.

Clusters are distributed in matrix, where atoms are arranged more randomly. The degree of topological ordering is different for various liquid metals and depends on temperature. In some cases clusters are the elements of fractal structure, whose topological ordering is another than in typical disordered systems. With heating the size of clusters decreases and the structure attempts to have less fraction of inhomogeneities.

There are various methods for determining of cluster size. Beside diffraction data, results on small angle scattering, the thermodynamic data also allow to estimate the cluster size. For instance the heat of evaporation (ΔQ_{EVA}) and melting (ΔQ_{Melt}) are in relation with cluster size value [3-5]:

$$R_{\text{Cl}} = (\Delta Q_{\text{EVA}} / \Delta Q_{\text{Melt}}) \beta^{1/3} r_s \quad (1)$$

where $\beta = 3Z \alpha_{\text{cl}} / 4\pi$ (Z - number of neighbours difference for crystalline and molten structure; α_{cl} - coefficient depending of clusters shape and atomic packing in it).

We have calculated R_{Cl} according to this formula for above listed metals used in determination of TRP. Obtained data are compared with cluster size values, estimated by other methods. Such comparison confirms the clusters structure of these liquid elements and existence of individual features in this structure for any of them.

Obviously those due to some degree of ordering configuration of entropy for melt S_{CONF} , should be changed significantly with heating, approaching to value for random atomic distribution. Analytical relation between S_{CONF} and $g(r)$ has a form:

$$S_{\text{CONF}} = -2\pi R N/V \int_{r_{\text{min}}}^{R_{\text{cor}}} g(r) \ln(g(r)) r^2 dr \quad (2)$$

where R - gas constant; $N/V = \rho_0$ - mean atomic density.

Reasonably to assume that upper limit of integrating in (2) is the same that correlation radius whereas the downer one is minimum position before principal peak in $g(r)$.

Dependence of $S_{\text{CONF}} = f(T)$ for In and Al has in fact the linear behaviour, that monotonic transformation of microhomogeneous structure into more homogeneous due to cluster drilling.

In case of tin S_{CONF} is almost unchangeable at low temperatures. It rapidly changes with heating showing the slope at the temperature when the shoulder in $g(r)$ disappears.

More complicated dependence (compared, for example, with Al) is observed for liquid gallium: within first interval just after melting the entropy shows a slight increase up to $T \approx 400$ K and then decreases with possible slope at over heating by 500 K, which is also in correlation with diffraction data. By the way it should be noted that in vicinity of $T = 400$ K for Ga the anomalous behavior in thermal physical properties (thermopower, density) temperature dependence was observed [6, 7].

Therefore, the structure and thermodynamic studies reveal the some individual features for each melt. Certainly that temperature dependence of parameter obtained from structure data and thermodynamic characteristics also reveals the individual features, which influence the crystal formation processes.

The structure transformation features in liquid metals should be considered as basis in studying of phase transitions, determining the characteristics of TRP.

3. Thermal physical processes and temperature fluctuations near crystallization front

It is known that for casting and for other practical use the temperature measurements with accuracy less than 0.1 K is needed occasionally. But there are some technical problems in thermometry where the significantly highest accuracy is needed. On that reason the detail studying of processes which occur on the border of liquids and solid phase should be started from solving of some particular problems.

High-precision experimental measurements of temperature as function of duration at crystallization of reference point metals at conditions maximally near equilibrium ones show the deviation from horizontal plateau shape. Particularly, this dependence is step like [2]. The steps are small (0.5-1.0 mK) but its height is large than error of measurements. The number of such steps was equal 2 or 3. Besides it is shown that overheating of molten In and Sn lead to increase of supercooling depth before crystallization. This phenomenon is not completely studied, but exists the assumption about deactivations of admixture, which could be the nucleus. This assumption is not free from limitations because the mechanism of deactivation is unclear.

With cooling of disordered melt it is of most probability that start of ordering can occur in form of fractal clusters, which due to its branched structure need less number of atoms for the creation of the same radius structure unit. With increase of fractal size the bonds between them become stronger. With further growth of fractal clusters their size can to reach the values, corresponding to critical nucleus and then process transits into another stage - formation of giant percolation clusters, which occupies the total volume of metal.

Above mentioned mechanism of crystallization is similar to Chalmers model, but with important difference: noted series of structure transformations can not be continuous due to competition between processes.

Before the growth of initial fractal clusters is completed the competition between further cluster growth due to cluster-particle mechanism and cluster-cluster aggregation one occurs. Duration of such competition processes when the new phase growth can be considered as first crystallization stage.

The next stage of scale hierarchy is characterized by competition of nucleus with formation of grain structure at cooling.

Finally, during the last scale of crystallization all the structural units with dimension less than 3 (doping none crystalline structural units) remove into intergrain band of crystalline structure and exist in structural dense state due to compressing forces of stressed grains.

Irreversibility and difference (un-similarity) of melting-crystallization processes we have observed at experimental investigation of electron properties in vicinity of phase transition. The temperature dependence of absolute thermopower at heating and cooling for Ga and Bi is shown in Fig. 1.

Following from Ioffe-Regel suggestion about the major role of short range order in formation of electron properties we have calculated the thermopower with using of one electron approach, for which Mott formula has a simple form:

$$\alpha_F = -2,45 \cdot 10^{-2} \cdot T/E_F \quad (3)$$

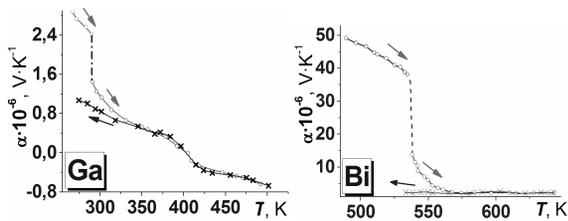


Fig. 1. Temperature dependence of thermopower in near-crystallization temperature region

It was founded that for Ga and Bi α_F value is in accordance with experimental ones at temperatures higher than upper hysteresis limit, that we attribute to complete creaking of covalent bandings. In this case of cooling the associate-clusters start the in formulation via covalent bonding only with starting of crystallization process.

Therefore, the crystallization starts only at T_{FT} (or lower) and the entropy producing at energy dissipation is governed factor of structure formation process.

Contrary to local processes of nucleation at crystallization the melting process occurs at T_{FT} isothermally at all intercrystalline grains and complete in liquid state when clusters disappear.

The crystallization at equilibrium thermodynamic conditions in case of massive metal is unattainable commonly ideal process. If even the overcooling temperature in heat removing direction is small, it is accompanied with thermal, convection over entire melt volume. We consider the influence of this convection in macroscopic and microscopic scale.

Certainly, that most undesirable deviation from equilibrium crystallization condition is related with overcooling of melt. In casting this factors should be avoided and three methods are used for it: holding the very close to equilibrium conditions of crystallization; the modification of melt; applying of fields (magnetic, electromagnetic, acoustic, etc.).

Another reason of deviation from typical plateau shape in crystallization curve is the convection process, which is relation with viscous properties of melt.

Hydrodynamic calculations of thermal convection in limited volumes are very complicated and can be realized for ideal systems only. Nevertheless it is established by experimental way that horizontal gradient of temperature can to reach $1 \text{ K}\cdot\text{cm}^{-1}$, promoting the convective flow of near boundary melt, what is accompanied by temperature fluctuations.

Occurrence of melting-crystallization phase transition and its use as temperature reference point was studied in In-Ga-Sn eutectic melt. The measurements were carried out in cell of own construction.

By means of thermoelectric batteries, installed along the perimeter of cylinder reference cell with melt and thermoresistive stabilizer of temperature the stable radial thermal temperature gradient was maintained.

Fig. 2 represents the thermograms of crystallization and melting, characterizing the temperature cell. The cooling curve is characterized by temperature fluctuations about $\pm 0.2 \text{ K}$. Analysis of fluctuations indicates their local formation at the crystallization front with following partial damping in reference cell. Fluctuations decrease with reducing of heat removing rate is lower then error of measurements, indicating the convective origin of these fluctuations. The curve corresponding to heating process is monotone over all plateau length, showing the accordance with above described mechanism of transition to molten state.

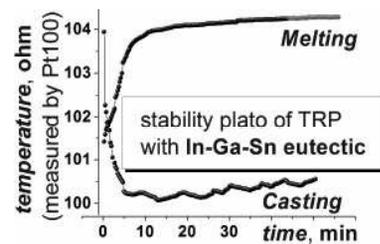


Fig. 2. Thermograms of crystallization and melting of used TRP

4. Conclusions

Non-reproducibility of temperature fixpoints exist due to some reasons: no accounting the structural - thermodynamic state of melt; mass-heat processes are not enough taken into account. It is fixed, that the temperature fluctuations (and non-stability of crystallization plateau) are of two types: small fluctuations (up to (1-2) mK) are caused by phases (stages) of crystallization process; major fluctuations (at us: $\pm 0.2 \text{ K}$) crystallizations are caused convective streams at the front. Fluctuations can be essentially reduced by approach to requirements of thermodynamic balance, but their complete elimination - is problematic.

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