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Advanced Materials & Technologies in Precisive Temperature Measurements

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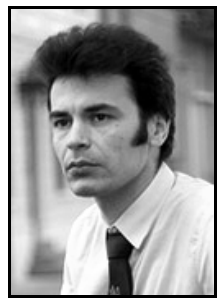

Areas of research activities: Structural studies of melts (liquid metals, molten alloys of different kind phase diagrams); Phase transitions in solids (structural aspects); Structure and thermodynamic properties of alloys; NDT; Thermodynamics - thermophysical properties of matter, Thermal analysis, Mathematical and numerical modelling of heat and mass transfer phenomena; Thermal metrology. Number of works, published in scientific journals and conference proceedings 140.

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Abstract

The studies of eutectic melts Cd-Sn, Bi-Cd are carried out be means of X-ray diffraction, metallography and differential scanning calorymetry methods in order to check the possibility to use them as temperature fix-point. It is shown that outside energetic influence on melt can change some parameters of structure and physical properties.

Keywords: Cd-Sn, Bi-Cd eutectic melts, X-ray diffraction, differential scanning calorymetry, temperature fix-point, energetical treatment.

Zaawansowane materiały i technologie w precyzyjnych pomiarach temperatury

Streszczenie

Stopy eutektyczne Cd-Sn, Bi-Cd badane były metodami dyfrakcji rentgenowskiej, metalografii oraz różniczkowej kalorymetrii skaningowej w celu uzyskania wiedzy o możliwości używania ich jako temperaturowych punktów odniesienia. Wykazano, że zewnętrzna obróbka energetyczna stopów zmienia ich parametry strukturalne i właściwości fizyczne.

Słowa kluczowe: stopy eutektyczne Cd-Sn, Bi-Cd, dyfrakcja rentgenowska, różniczkowa kalorymetria skaningowa, temperaturowy punkt odniesienia, obróbka energetyczna.

1. Introduction

It is of great importance to have a methods for precisive temperature measurements. With progress in technique the requirements to accuracy of temperature measurements also growth reaching the values, which are available with using of periodically verified thermometer only. On that reason it is needed to design the secondary fix point, whose main functional material has a following characteristics: high corrosive resistivity, high thermal capacity and thermal conductivity, stability of melting↔crystallization temperature and stability of thermal energy at phase transitions, low volatility and others. Metallic eutectic alloys are the materials, whose main properties satisfy these requirements. Main feature of these alloys among other multicomponent systems is the existence of equilibrium between two solid and one liquid phases at some definite temperature. Any change of concentration, temperature or pressure lead to break of such equilibrium. This fact allows to use the eutectic alloys as temperature reference points.

In most cases of contact temperature sensors the principal requirement is the existence of termodynamical equilibrium. The use of liquid metals as a thermosensitive elements has a some preferences on that reason and allows to increase the range of measured temperatures. But the influence of crystalline destroying factor and doping effect on the stability of electron properties, determining the metrologic characteristics of temperature measuring elements are poor studied to present time.

Since the industrial use of thermotransformers suppose the various conditions the analytical description of surrounding influence on thermometric characteristics of sensors is impossible. In structural aspects the nonstability of thermoelectric characteristics of solid crystalline transformers can be explained by existence of high temperature defects (point and volume) as well as radiation damages, polymorphous transformation, recrystallization aging etc. Nevertheless all these factors are far from complete and there are many different reasons of errors at measurements at higher temperature, which can not be directly accounted [1].

2. Fundamental

One can think that structural nonstability of electric properties are in developing during breaking of crystalline cell at melting but really it is not observed and opposite situation occurs. Taking into account the structural studies it is possible to consider the liquid metal as a disordered system, whose atoms are no localized within some definite microvolume but show the diffusive migration without any activation over all volume of liquid [2]. The heating of melt is accompanied by lack of the rest crystalline like short range order, who dominates in atomic distribution near the melting point. The activation of translation motion of atoms with increase of interatomic distances become more significant at higher temperatures.

Therefore the heating of melt leads to formation of more perfect specific liquid like structure, which can be described with using of probability functions. This fact shows the principal difference between liquid and solid. For last the heating is accompanied by more intensive formation of the structural defects. On that reason the replication of melt's electron properties should be more reliable at higher temperatures contrary to opposite behaviour in solids. The most important reasons:

- residual thermal stresses are impossible in liquid as isotropic and labil system;
- radiation defects as well as point or volume ones have another their origin. They disappear with relaxation period, which is significantly less then electric properties measuring time;
- such reasons of instability in electric properties as recrystallization, aging and fatigue no occur in melts due to absence of long range order, which is responsible for their appearance;
- more complicated is the influence of impurities. It is known that metals in liquid state show the higher chemical activity. In order to depress the possible reactions the construction materials of corrosive resistivity (carbides, nitrides, carbonitrides, oxides) are commonly used. But very important is a fact, confirmed both by in theoretical and experimental way, that impurities more significantly effect the electric properties in liquid state than in solid.

Practical use of liquid metal temperature transformes is connected with: choosing of melt, whose thermal physical properties are required; the satisfying of construction materials to thermometric melts; technology of liquid metallic temperature sensors producing.

In order to measure the temperature in wide range the different reference points are needed. Especially, some problems appear in case of intermediate and higher temperatures. One of them is the chemical interaction between eutectic melt and construction materials. One of eutectic melt, which can be used in intermediate range of temperature is $Bi_{0,45}Cd_{0,55}$ alloy. Its melting temperature equals to 148°C. Equilibrium phase diagram (Fig. 1) reveals the extremely small solubility in solid state [3].

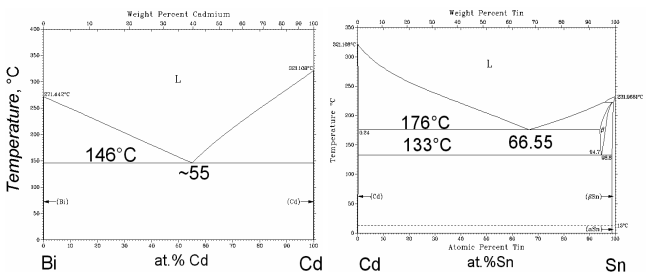

Fig. 1. Equilibrium phase diagram of Bi-Cd and Cd-Sn [3]
Rys. 1. Diagram stanu w strukturach Cd-Sn, Bi-Cd [3]

It was shown that structure of eutectic melt is characterized by existence of like kind atomic groups up to 250°C. The density dependence from concentration reveals the tendency to ordering in Bi-Cd alloys [4]. On other hand, there are no chemical compounds in equilibrium phase diagrams. Nevertheless, the thermodynamic data note the tendency to prefer interaction of unlike kind atoms. Enthalpy of mixing shows the negative deviation in comparison with regular solutions model [5].

Therefore the more detailed structure and physical properties studies are needed to understand the features of atomic distribution and interatomic interaction in this molten alloy. Similar situation is also for Cd-Sn eutectic melt.

3. Experimental

$Bi_{0,45}Cd_{0,55}$ alloy was prepared from pure Bi (99.9999%) and Cd (99.99%) by melting in vacuum furnace filled with argon X-ray diffraction studies were carried out with using a high temperature diffractometer with special attachment that makes it possible to investigate solids and liquid samples at different temperatures up to 1800K. The Breg-Brentano focusing geometry was used to obtain the diffraction patterns with high accuracy and resolution. The CuKα radiation was monochromatized by LiF single crystals, installed in the initial beam. The scattered intensities as a function of scattering angle were recorded within the range $1\cdot10^{10}$m<k<$7\cdot10^{10}$m, using a special electronic system. In order to obtain more accurate scattered intensities, the scan time was equal to 100s in the region of principal peak and 20s in the remaining parts of intensity curve. Compton scattering was taken into account before normalization of the intensity curves. This scattering was subtracted from the total intensity using the data presented in [2]. The diffracted intensity values were recorded using a NaJ(Tl) scintillator-detector in conjunction with an amplification system. The sample was placed in a rounded cup of 20 mm diameter. After the correction for incoherent scattering and polarization, the patterns were normalized by Krogh-Moe`s method. After this procedure, intensity functions were used to calculate the structure factors $S(k)$ and pair correlation functions $g(r)$. These functions were analyzed and main structure parameters were obtained from them.

Cd-Sn and Bi-Cd eutectic alloys was prepared from pure Sn (99.9999%), Cd (99.99%) and Bi (99.99%). Calorymetric studies of Cd-Sn were carried out by differential scanning microcalorymeter (DSC) [6]. The Percin-Elmer scanning microcalorymeter with heat flow compensation was used. The use of such equipment is motivated by necessarity of more precisive investigation of phase transition as a process with significant density of heat flow. In this case we are interested in obtaining of precisive profile of heart flow maxima. The accuracy in heat flow, obtained with using of this calorymeter was less than 3÷5%. The reiteration in measured results of supplied heat at phase transition in one measuring series was equal to ±1%. The accuracy in temperature measurement was ±0,1 K. The crucible with sample was heated fluently with linear heating rate in unit of large mass and stabilized axial heat flow. By means of resistance disk platinum termometer the temperature measurements were carried out as well as heat flow along both sample and etalon axis, what is needed their temperatures were equal.

One of studied in this work materials was the Cd-Sn eutectic alloys (Tmelt=449.2K). This alloy consists tin, which at crystallization transits from diamagnetic to paramagnetic state. The melt was crystallized in furnace of magnetometer with cooling rate 30 K/min in magnetic field of 800 kA/m strength and without it. We have analyzed also the changes in eutectic alloy, which were caused by outside energetic influence, by means of metalography and calorymetry.

4. Results and Discussion

The structure factor for liquid $Bi_{0,45}Cd_{0,55}$ eutectic alloy was obtained at temperature 5K above melting point (Fig. 2). In this figure are also presented the $S(k)$ for liquid Bi and Cd.

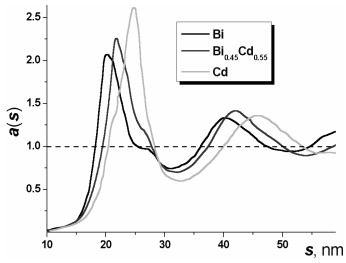

Fig. 2. Structure factor of Bi-Cd eutectic melt with comparison to ones components ($T=T_M$+5 K)
Rys. 2. Czynniki strukturalne ciekłej eutektyki Bi-Cd oraz jej komponenty w ($T=T_M$+5 K)

Comparison of these functions allowed us to note that $S(k)$ for eutectic melt is more similar to one of liquid Bi than for liquid Cd. One can see that shoulder on right hand side in $S(k)$ of Bi also appears on principal peak for eutectic melt. It can be seen also the position of first peak in $S(k)$ for eutectic molten alloy is closer to corresponding value by liquid Bi. The similar features are also observed in structure parameters, obtained from pair correlation functions. Most probable interatomic distance r_1 and number of neighbours Z_1 were used for model interpretation of structure data. Model of random atomic distribution and quasieutectic one were used. According to these models r_1 parameters can be written:

$$r_1^{\text{r.d.}} = \left(c_{\text{Bi}} r_{1.\text{Bi}} + c_{\text{Cd}} r_{1.\text{Cd}}\right) \cdot \left(c_{\text{Bi}} K_{\text{Bi}} + c_{\text{Cd}} K_{\text{Cd}}\right) \quad (1)$$

$$r_1^{\text{q.e.}} = c_{\text{Bi}} K_{\text{Bi}}^2 r_{1.\text{Bi}} + c_{\text{Cd}} K_{\text{Cd}}^2 r_{1.\text{Cd}} \quad (2)$$

where $r_1^{\text{r.d.}}$, $r_1^{\text{q.d.}}$ – most probable interatomic distances, calculated for model of random atomic distribution and quasieutectic one. c_{Bi}, c_{Cd} – fractions of Bi and Cd in alloy which for our melt equal to 0,45 and 0,55 respectively. $r_{1.\text{Bi}}$, $r_{1.\text{Cd}}$ – most probable interatomic distances for liquid Bi and Cd respectively.

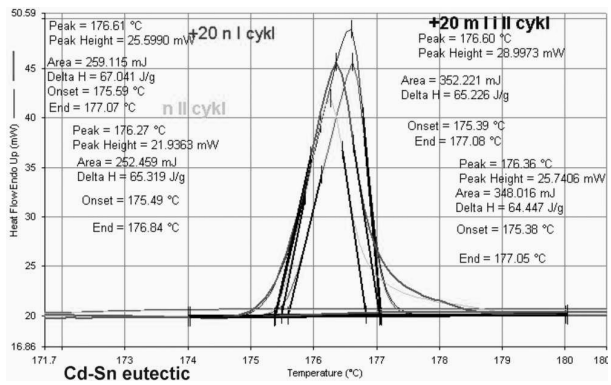

Fig. 3. Heat flow at melting eutectic alloy
Rys. 3. Ciepło właściwe topnienia eutektyki

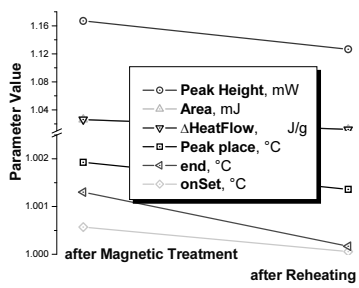

Fig. 4. Influence of energetic prehistory of heat flow for Cd-Sn eutectic alloy at phase transition solid-liquid
Rys. 4. Wpływ energetycznej prehistorii na ciepło właściwe topnienia eutektyki Cd-Sn w trakcie przejścia fazowego solid-liquid

The results on studies of magnetic field influence of eutectic Cd-Sn molten alloy are represented. This alloy is considered as promising for temperature fix-point (reference point). Such fix point can be used in mobile reference systems for checking of thermocouple thermometers and resistivity ones [7]. This work is in frame of more wider project on determination of outside energetic influence on the change of eutectic melting plateau reproducing [8, 9].

Early it was shown by means of metallography the existence of significant changes of homogeneity in this eutectic alloy due to applied magnetic field. These changes are caused by Sn-clusters, which exist in melt. Nonequality in values of energy supplied during crystallization in magnetic field treated and untreated samples is confirmed by calorymetry analysis. The observed changes in heat energy at melting indicate the less changes at thermal cycling of magnetically treated sample.

It should be noted also that parametrs of heat flow for sample treated by magnetic field and normalized via overheating evidently indicates the existence of sensitive from metrology point of view changes in plateau shape dyring phase transition. Particularly the change of height and square under maximum definitely is displayed in plateau stability for used phase transitions.

5. Conclusions

Obtained results allowed us to conclude that use of multicomponent metallic systems at temperature reference point is connected with complex studies of main physical properties and structure near meltnig point both in liquid and solid state.

In the structure inhomogeneities in Bi-Cd and Cd-Sn eutectic melts before solidification points and possibility to effect them by means of outside energetic treatment should be taken into account at construction of termosensitive systems.

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