INVESTIGATION OF THE SOLID-LIQUID PHASE TRANSITION FOR SnIn ALLOYS BY THE POSITRON ANNIHILATION METHOD

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The monovacancy formation energy in Sn-17 wt.% In and Sn-32 wt.% In was determined on the basis of the temperature dependence of the peak counting rate for these alloys. A sudden increase in the counting rate was observed between solidus and liquidus temperature. This phenomenon is connected with the formation of large defects acting as positron traps.

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1. Introduction

As it is proved by positron annihilation (PA) investigations the behavior of pure tin and indium during the heating to the melting point (T_M) and during the melting is different. The peak counting rate, $F(T)$, for solid indium changes by about 8 percent between room temperature and T_M , but at T_M the $F(T)$ parameter increases by no more than 1-2 percent [1, 2]. Positron lifetime for In at T_M decreases by about 2 percent [3]. On the contrary, for pure tin the changes of the annihilation parameters are rather insignificant in the solid state whereas at T_M sudden increase of both $F(T)$ [2] and Doppler broadening S parameter [4] is observed. Thus, it may be concluded that in solid tin the positrons are weakly trapped by the monovacancies, while indium-monovacancies trap positrons strongly.

Monovacancy formation energy, $H_{V_1}^F$, for pure tin and indium was determined with the use of PA method by many authors. The values of $H_{V_1}^F$, obtained by different PA techniques for indium, collected by Weiler et al. [5], are between 0.43 and 0.59 eV. For tin $H_{V_1}^F$ was determined mainly from the so-called threshold temperature T_T and is equal to about 0.5 eV [4, 6, 7]. The phase diagram of Sn-In alloy is simple, but the structure and the melting process of Sn-rich samples are rather complicated [8]. The coexistence of amorphous and crystalline phases was observed in sub-microcrystalline solid samples. Thus it may be interesting to know how the various mechanisms of positron trapping for pure metals are reflected in

the chosen Sn-In alloys: Sn-17 wt.% In and Sn-32 wt.% In. The first one has one phase (γ) in the solid state, and the second one exhibits the two-phase ($\beta + \gamma$) structure in the solid state.

2. Experiment

The samples were prepared by melting the granulate of the 4N pure tin and indium in the rectangular measuring vessel. The heater was placed on the one side of the vessel while at the opposite side the titanium foil (8 mm thick) window was mounted. In this way positrons from ^{22}Na source penetrated to the inside of the sample through the window. After melting the sample was stored for 5 hours at 400°C . Next, during slow cooling, step by step, the peak counting rate, $F(T)$, was measured. At each temperature the number of coincidence accumulated, during the time of 2 hours, was of the order of 5×10^4 . After that, the angular correlation curves (AC) were measured at the room temperature (RT), near the solidus temperature (T_S) in the solid phase and above the liquidus temperature (T_L). They were 135°C and 215°C for Sn-17 wt.% In and 112°C and 185°C for Sn-32 wt.% In, respectively. All measurements were performed in the protective argon atmosphere under the atmospheric pressure. Temperature was controlled by NiCr-Ni thermocouple with an accuracy of $\pm 1^\circ\text{C}$. The details of the apparatus are described in [9]. Positron lifetime spectrum was measured at the RT for a well-annealed Sn-17 wt.% In sample with the use of a conventional fast-slow spectrometer with resolution function (FWHM) 310 ± 5 ps.

3. Results and discussion

Figures 1b and 2b show the results of the measurements of the temperature dependence of the peak counting rate for Sn-17 wt.% In and Sn-32 wt.% In samples, respectively. For clarity, the same results are figured in Figs. 1a and 2a, but they are in the greater scale on the T -axis between RT and 250°C . Solidus and liquidus temperatures marked in the figures are taken from a phase diagram of Sn-In alloy, presented in Ref. [8]. As we can see, in the range from RT to T_S , the value of $F(T)$ increases insignificantly. It was assumed that this results from positron trapping at monovacancies. Simple trapping model [10] was used to obtain monovacancy formation energy from the formula

$$F(T) = \frac{F_0 + AF_v \exp\left(-\frac{H_{V_1}^F}{kT}\right)}{1 + A \exp\left(\frac{H_{V_1}^F}{kT}\right)}, \quad (1)$$

where F_0 is the average value of $F(T)$ near RT, F_v is the average value of $F(T)$ near T_S , k — Boltzmann constant, $A = \mu\tau_f \exp(S_{V_1}^F/k)$ with τ_f — positron lifetime in the bulk, $S_{V_1}^F$ — monovacancy formation entropy, μ — positron trapping rate per unit vacancy concentration.

Best fitting curves (solid lines in Figs. 1a and 2a) were obtained for $H_{V_1}^F = 0.52 \pm 0.06$ eV and $A = (1.4 \pm 0.6) \times 10^7$ for Sn-17 wt.% In. Corresponding values

Fig. 1. Temperature dependence of the normalized peak counting rate for Sn-17 wt.% In alloy in 0–250 K (a) and 0–400 K (b).

Fig. 2. Temperature dependence of the normalized peak counting rate for Sn-32 wt.% In alloy in 0–250 K (a) and 0–400 K (b).

for Sn-32 wt.% In are 0.54 ± 0.04 eV and $(1.7 \pm 0.5) \times 10^7$, respectively. The values of HV_1^E for investigated alloys are comparable with monovacancy formation energy for both pure tin and indium. The obtained values of A are larger than for most metals [11]. Nevertheless, they are of the same order as for pure In [5, 11, 12]. It is an indication that in the investigated alloys positrons are trapped at the In-like monovacancies in the solid phase.

From the RT positron lifetime spectrum for the Sn-17 wt.% In alloy, after the extraction of contributions of positron source and kapton foil, one component was obtained with $\tau = 187 \pm 1$ ps. This value is nearer to the bulk lifetime in pure

In (192 ps [5]) than in pure Sn (202 ps [13]). Angular correlation curves for pure In and Sn and for the investigated alloys were normalized to the same area. Next, the R parameters were calculated in the similar way described by Triftshäuser [1]. AC curve measured at RT was taken as a reference. The values of the R parameter were calculated taking into account the area under the peak-part of AC (from 0 to 2 mrad) and under the wing-part of AC (from 8 to 12 mrad). For pure metals in calculating the R parameter, AC curves measured in RT (somewhat below and above T_M) were used. The R parameter characterizes the size of the positron trap center. For the alloys the corresponding temperatures were RT, near T_S (solid phase) and above T_L (liquid phase), respectively.

The determined values of the R parameters are collected in Table.

TABLE
The values of the R parameter for solid and liquid Sn, In and their alloys.

Phase	Sn	Sn-17 wt.% In	Sn-32 wt.% In	In
Solid	0.3 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	1.7 ± 0.1
Liquid	2.4 ± 0.1	1.8 ± 0.1	1.9 ± 0.1	2.0 ± 0.1

As we can see from Table the size of the trapping center in liquid phase of Sn and its alloys is larger than that in the solid phase. The nature of these centers is unknown. Nevertheless, it is worth mentioning that during the melting process the behavior of pure Sn and investigated alloys is similar to that of Ga. For Ga positron lifetime increases from 190 to 260 ps [14] and $F(T)$ parameter by about 10 percent [9] during the melting. Recently Gramsch et al. [15] have reported a drastic drop in the positron diffusion length for Ga from 1200 ± 100 Å (solid) to 60 ± 5 Å after melting. All these facts together with the tendency of Sn and Ga to overcooling may indicate that in these liquid metals positrons are trapped at the similar centers as in solid metallic glasses.

4. Conclusions

From PA measurements for Sn-17 wt.% In and Sn-32 wt.% In alloys the following picture of positron trapping may be deduced. In the liquid phase positrons are trapped in large defects (clusters). During the solidification, when solid Sn-rich crystals grow, those centers rapidly vanish. Near the solidus temperature, when the volume of crystal containing In increases, and In-content increases in them as well, positrons are trapped mainly by monovacancies, which trap positrons also below the solidus temperature. Monovacancy formation energy equals 0.52 ± 0.006 eV and 0.54 ± 0.04 eV for Sn-17 wt.% In and Sn-32 wt.% In, respectively.

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