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Melting Process of the Sn–45 wt.% In and Sn–77 wt.% In Alloys as Viewed by Positron Annihilation

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The temperature dependences of the positron annihilation parameters F and R were determined for Sn–45 wt.% In and Sn–77 wt.% In alloys. The obtained results enabled to verify the vacancy and the quasicrystalline models of the melting process. It was found that for metals transforming into the liquid state from the structures different than the close packed structure, the melting transition are hardly explainable in terms of the vacancy model of melting. The strong trapping of positrons in metallic liquids is an indication of the presence of microvoids (vacancy clusters) or microcrystals containing defects more immense than vacancies. The share of these positron trapping centers in the volume of metallic liquids is constant or decreases with increasing temperature. The obtained results demonstrate the particular applicability of the positron annihilation method for studies of defect kinetics in metallic liquids.

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1. Introduction

The phenomenon of melting of metals and alloys belongs to the class of long-standing, fundamental problems in metallurgy. Despite of very intensive research efforts up to now there is no quantitative theory, which can explain all the details of the melting process in satisfactory agreement with experimental data [1, 2]. Elaboration of such a theory requires the application of appropriate models of both the solid and the liquid states. While for the solid state such model already exists, there is no commonly accepted model of the liquids, satisfactorily describing their structure and properties and sufficient to enable the formulation of satisfactory theory or at least a model of melting process.

From the point of view of the spatial distribution of their constituent atoms or molecules, liquids occupy an intermediate position between solids and gases. Therefore, most of the hitherto existing theories and/or models of the liquid state

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tend to bring into evidence its similarity to the solid, or alternatively, to the gaseous state.

The experimental data on the changes of many of the physical properties of passing from the solid to the liquid state, e.g. slight changes in the specific heat and in volume, as well as the fact that heat of melting is $30 \div 40$ times smaller than that of vaporization, irresistibly suggest the existence of a similarity of the structure of melt just above the melting point to the structure of the mother solid. Therefore it is not surprising that many researchers exploited this similarity in their attempts to formulate different theories or models of the melting process [3, 4].

The theories mentioned above tend to connect the melting process with the crystal lattice instability caused by generation of various crystal lattice defects. For example, the authors of papers [4–6] tried to interpret the melting process as the process of spontaneous generation and proliferation of dislocations.

Another theory of the melting process, invoking the crystal lattice instability, is the "hole" theory of liquids proposed by Frenkel and intensively developed by Eyring and Mu-Shik [7, 8]. The quantitative version of this theory has been presented at the end of seventies by Górecki [9] as the vacancy model of melting. The Górecki vacancy model of melting describes the solid-to-liquid transformations as a spontaneous generation of vacancies in the crystal lattice at the cost of the heat of melting, identified with the formation energy of all the vacancies generated during the melting process. The avalanche generation of vacancies starts after reaching a definite temperature (melting point) at which the concentration of equilibrium vacancies in the solid state reaches a critical value of about 0.37 at.%, the same for all the metals, whereas the increase in the vacancy concentration on passing to the liquid state amounts ≈ 10 at.%.

The quasicrystalline model of liquids [10] assumes that after melting the liquid contains numerous microcrystals with the short-range ordered structure similar to that just before melting. Their dimensions and number diminish with increasing temperature till a complete disappearance at temperature much higher than the melting point ($\approx 1.75 \div 1.85 T_{\mathrm{m}}$).

The application of the positron annihilation method for studying the crystal lattice defects is based on the phenomenon of positron trapping in the defects. The measurable changes in the positron annihilation parameters due to the trapping in vacancies occur in the interval of changes in the vacancy concentration ranging from 10^{-7} to 10^{-4}. At concentrations of vacancies higher than 10^{-4} the saturation of positron trapping in vacancies occurs and no changes in the positron annihilation are observed.

According to the vacancy model of melting [9], for metals with close packed structures $A1$ and $A3$ the saturation effect should occur below the melting point, because at the melting temperature T_{m} the vacancy concentration reaches a value of the order of 10^{-3}, i.e. much higher than the saturation limit. Further increase

in the vacancy concentration (by a factor of more than 30) in the melting process should not affect the positron annihilation parameters. This has been confirmed by numerous investigations of the temperature dependence of the positron annihilation parameters, aimed to the determination of the vacancy formation energy in metals, as well as by few experiments in which these dependence were measured on passing through the melting point.

An example of the behavior conformable with the predictions of the vacancy model of melting [9] are the simple metals like Cu [11], Ag [12, 13] and also Pb and In [14]. For these metals the peak counting rate increases by $\approx 30\%$ due to the increase in the specific volume below the melting temperature and in the liquid state remains nearly constant, which is typical of positron annihilation saturation. The behavior of the positron annihilation parameters in pure Sn and Ga is completely different. Shah and Catz [15] observed for these metals a sharp increase in the line shape parameter S at melting temperature, T_{m}, and linearly decreases with increasing temperature in the liquid phase. Similar changes of the peak counting rate has been observed for Sn in [16]. Further indication of the change in the annihilation mechanism in Sn on passing through the melting point is the shortening of the diffusion path of positrons in Sn on melting from 720 Å in the solid to 320 Å in the liquid phase [17]. The shortening of the diffusion path on melting of Ga is even more evident [17]. Taking into account that the changes in the specific volume on passing through the melting point are for Sn and Ga of the different sign, and the peak counting rate increases at T_{m} by 4% for Sn [15, 16] and by 18% for Ga [18], one must conclude that for these metals the changes in the positron annihilation parameters at T_{m} are not caused solely by the changes in the specific volume. The Sn–In alloys are very suitable for studies of the solid–metal liquid phase transition by the positron annihilation methods, because in pure Sn the positrons are trapped rather weakly but on passing through the melting point a sudden increase in the peak counting rate is observed [15, 16], in contrast to pure indium, which behaves like metals with close packed structures [14] in both the solid and liquid phases.

The aim of the present study is to compare the predictions of the vacancy and the quasicrystalline models of melting with the results of the measurements of the positron annihilation parameters, sensitive to the kind and concentration of crystal lattice defects, in both the solid liquid phases of metals and alloys.

2. Experimental

The samples of Sn alloys with 45 and 77 weight percents of In 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 site the titanium foil (8 μm thick) window was mounted. In this way positrons from ^{22}Na source penetrated to the inside of the sample through the window. The samples were placed on the axis of the spectrometer in the gas

tight chamber filled with dry, oxygen-free argon under pressure slightly exceeding the atmospheric pressure. The detailed description of measuring system could be found in [18].

After melting, the samples were annealed for 24 hours at 460°C. Next, during slow cooling, step by step, the peak counting rate (F parameter) was measured by the time of 2 hours. At each temperature counts of the order of 5×10^4 were collected. After that, the angular correlations of two quantum positron annihilation (angular correlation of annihilation radiation, ACAR) curves were measured at different temperatures first for the liquid and then for the solid phase. Before each ACAR measurement the samples were carefully tempered at each temperature with the aim to achieve the thermal equilibrium. The temperatures at which the ACAR curve for alloys were measured have been chosen on the basis of the phase diagram of the binary In–Sn system and our previous measurements of coincidence peak counting rate (F parameter). For each alloy the last ACAR measurement in the liquid phase and the first measurement in the solid phase have been performed at temperatures slightly higher than the liquidus and slightly lower than the solidus temperature, respectively. The last ACAR determination has been performed at room temperature (RT).

3. Results and discussion

The temperature dependences of the F parameter for In–Sn alloys containing 45 and 77 wt.% of In are shown in Figs. 1 and 2, respectively. The inset of Fig. 1 represents the temperature dependence of the F parameter for pure In, the inset of Fig. 2 — for pure Sn.

The values of the R parameter given in Table were calculated by the following formula [14]:

$$R = \frac{H_T - H_{\mathrm{RT}}}{A_T - A_{\mathrm{RT}}}, \tag{3.1}$$

where H_T and H_{RT} were calculated taking into account the area under the central part of ACAR from 0 to 4 mrad measured at a given temperature and in RT, respectively (well-annealed samples); A_T and A_{RT} — area under the wing part of ACAR (from 8 to 12 mrad).

From the data of Fig. 1 and from the values of vacancy formation energy determined in [19] it can be concluded that the increase in the F parameter value with increasing temperature could be ascribed to the annihilation of positrons trapped in vacancies. In accordance with the vacancy model of melting, the saturation of positron annihilation has been observed below the solidus temperature, T_{S}.

In the case of alloys, in the temperature interval ranging from the solidus, T_{S}, to the liquidus, T_{L}, temperature, where the liquid and solid phase coexist, the positrons are trapped in vacancies and their agglomerations. This is evidenced by small changes in the R parameter value on passing from the solid to the liquid phase for all the alloys containing less than 50 wt.% of In [19]. Insignificant changes

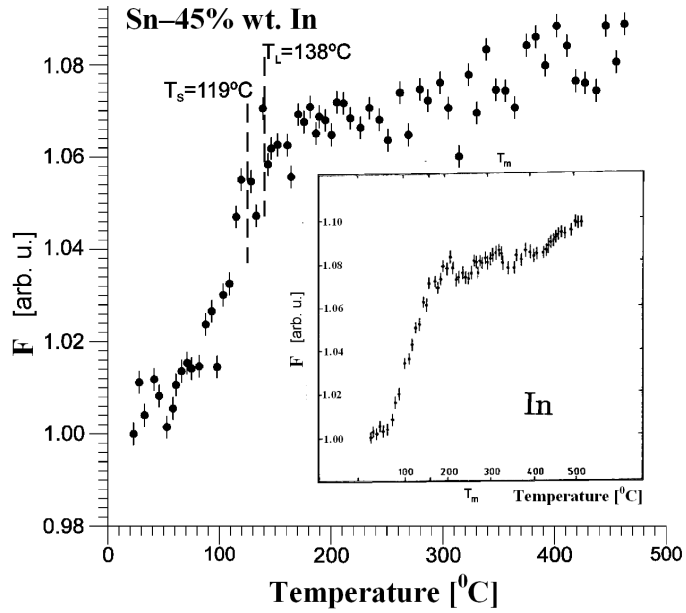

Fig. 1. Temperature dependence of the coincidence counting rate (relative to that measured at RT) at the maximum of ACAR curve for the Sn–45 wt.% In and pure indium samples. T_{S}, T_{L}, and T_{m} denote the solidus, liquidus, and melting temperatures, respectively.

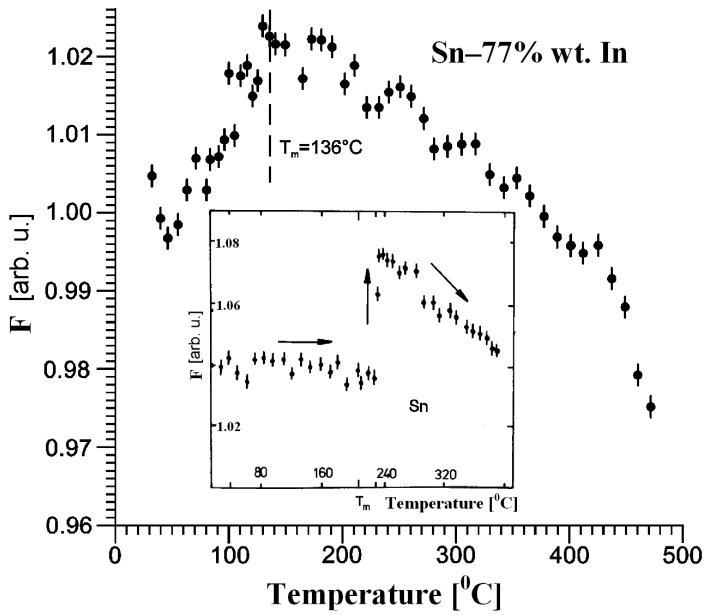

Fig. 2. The same as in Fig. 1 for the Sn–77 wt.% In and pure tin samples.

TABLE

Values of the R parameter for solid (S) and liquid (L) phases of In and Sn and their alloys.

Sample composition	Temperature [°C]	R
In	140 L	1.7±0.1
	180 L	2.0 ± 0.1
	460 L	2.5 ± 0.1
Sn–45 wt.% In	110 S	1.5 ± 0.1
	150 L	2.5 ± 0.1
	460 L	2.7 ± 0.1
Sn–77 wt.% In	120 S	6.9 ± 0.1
	140 L	10.5 ± 0.1
	460 L	2.7 ± 0.1
Sn	225 S	0.26 ± 0.05
	240 L	2.35 ± 0.05
	330 L	0.92 ± 0.05

of the F parameter value in the liquid phase of each alloy evidence that the defects created during the melting process are stable up to temperature of 500°C and that just these defects are the reason of the annihilation saturation. It is, however, difficult to decide whether the trapping centers are, in accord with the vacancy model of melting [20, 21], the vacancy agglomerations, trapping the positrons more efficiently than single vacancies or the defects connected with microcrystals whose presence is assumed in the quasicrystalline model of the liquid state. In pure In and Sn the share of the monocrystals in the volume of melt just after the melting amounts 31% and 23% respectively. The complete decay of the microcrystals occurs at temperature of 650−700°C [10].

The starting point for discussing a distinctly different course of the temperature dependence of the F parameter for the liquid phase of alloy containing 77 wt.% of In are the changes of the R parameter value for pure Sn and In and for alloy containing 45 wt.% of In. For pure In, in full accordance with the Triftshäuser data [14], the value of R parameter practically does not change, thus suggesting that the positron trapping centers in both the solid and liquid phases are the same. The same could be stated in the case of the alloy containing 45 wt.% of In as well as all the formerly investigated alloys containing less than 50 wt.% of In [19]. For pure Sn the value of the R parameter markedly increases on passing from the solid to the liquid phase. For alloy containing 77 wt.% of In this increase is even more evident, similarly as other Sn–In for alloys containing more than 50 wt.% of In, investigated formerly [22, 23].

The most intriguing fact is that in the liquid phase the R parameter value decreases with increasing temperature, thus implying that in Sn and Sn–In alloys

containing more than 50 wt.% of In the positrons are trapped in defects other than vacancies. It is difficult to decide in what extent these defects are associated with the presence in the liquid phase of the Sn(II) microcrystals which disintegrate completely at temperature higher than 400°C [24]. Independent of the kind of the centers responsible for positron trapping in the solid phase, it seems to be reasonable to assume, according to the quasicrystalline model of liquids [10], that the decrease in the F parameter value with increasing temperature is caused by changes in both the number as well as in dimensions and in the structure of short--range-ordered microregions. These changes occur up to temperatures close to the boiling point, where the microcrystals disappear and the liquid becomes completely structureless. The convergence of the data on the stability of the monocrystals in the liquid phases of In [10] and Sn [10, 22] is a further indication of the possible relation of the positron trapping centers to the presence of the microcrystals in the liquid phase.

It is difficult to explain the dissimilarity of the course of the temperature dependence of the F parameter for alloys containing less and more than 50 wt.% of In basing on the results of measurements performed in the present study. Probably, this dissimilarity results from the differences in the bonding energies of the In–In, In–Sn and Sn–Sn pairs in the liquid phase. Nevertheless, it is clear that in the Sn–In alloys containing more than 50 wt.% of In, the positrons are trapped in defects other than vacancies. The occurrence of these defects is associated with the presence of Sn microcrystals in the liquid phase. In alloys of nearly eutectic composition they are particularly stable and do not disintegrate even after prolonged tempering of the sample [22].

4. Conclusions

The results of the present study demonstrate that the nature and dynamics of strong positron trapping centers forming during the melting of metallic materials could be described in the frames of both the vacancy and quasicrystalline models of the molten state. The suggestions that these centers are the vacancy clusters may be checked by systematic investigations of the eventual changes in the positron lifetimes spectrum in molten materials with changing their temperature. Probably, this way it will be possible to discriminate between the vacancy and quasicrystalline models of the molten state metals and alloys.

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