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CONTRIBUTION TO PHASE DIAGRAM INVESTIGATION OF Pb–In BINARY SYSTEM

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Abstract

Experimental results obtained by phase diagram investigation of Pb–In binary system are presented in the paper and compared with literature data. Liquidus and solidus temperatures, as well as cell parameters were determined, and structural analysis of this system was made. Microstructural analysis was done by SEM-EDX, crystallographic analysis was performed by diffractometry, while liquidus and solidus temperatures were determined by DTA. Obtained results show that in investigated system exist three areas: area reach in In, area reach in Pb and separating the intermediate phase (αIn). Experimental results show good agreement with literature.

Keywords: DTA, Pb–In alloys, phase diagrams, SEM-EDX, X-ray analysis

Introduction

Even nowadays unleaded solder are matter of different investigations lead alloys still inspire interest in some area of science and technology [1, 2]. The phase diagram of the Pb–In system, has been considered by a great number of investigators. Based on thermal investigation, Kurnakow [3] defined the liquidus line for whole concentration area and concluded that the liquid solution has enlonged range. According to the thermal investigation and X-ray analysis, Agreew [4] defined the liquidus line for the concentration range of 30–40 mass% Pb. These two authors identified two-phase area in which the In based phase and Pb based phase are in the equilibrium, from which the last one transforms peritectically at 154°C. Valentiner [5] established the existence of solid intermediate (αIn) phase formed peritectically at 171.9°C. Subsequently, the other investigators, Klemm [6], Campbell [7], Oelsen [8], Raynor [9] and Valentiner [10], also defined the liquidus and solidus lines and confirmed the existence of intermediate phase. Heumann [11] except thermal and X-ray investigations, performed electrical resistance measurement for complete concentration range and confirmed peritectical temperature. Superconductivity of this system for –27 to 40°C

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temperature range was measured by Nebach [12]. Liao [13], Evens [14] and Marcotte [15] determined the liquidus and solidus temperatures by DTA. Presently time this binary system was investigated by Nabot and Ansara [16] and the authors of this paper [17]. Lattice parameters at room temperature were determined by Ageew [4] and Valentiner [5], who noticed that linear parameters decrease regarding to composition. The samples of Pb–In system, annealed for three months at 150°C and quenched, were investigated by Tyzack [18, 19] using X-ray diffraction. These results show that *c*/*a* ratio rises with Pb concentration approximately to ≈12% Pb. The lattice parameters in the concentration area of 7–14 mass% Pb were determined by Moore [20] using high temperature diffraction. In the literature exist a lot of data concerning properties of this binary system (especialy thermodynamical data [21]).

Experimental

The samples, used in the experiments were prepared from pure Pb and In. The samples had constant volume of 0.2 cm^3. DTA apparature and experimental technique are describer applied in literature [22, 26]. Scanning electronic microscopy was carried out on electronic microscope Philips Xl – 300 with EDX from EDAX, with resolution of 1 nm (30 kV) and 5 nm (1 kV), exciting voltage 0.2–30 kV, enlargement of 500000X and detector for secondary and back electrons. Diffractometry was used for structural investigation. Samples (in the form of metallic plates) were investigated using diffractometer Philips PW1710 under following conditions: radiation from copper anticatode with CuK_α=1.54178 Å and graphite monocromator, working voltage U=40 kV, current strength I=30 mA. Samples were investigated in the range of 2θ 4–90° (with step of 0.02° and time 0.8 s).

Results and discusion

Phase diagram

The results of former liquidus and solidus temperatures experimental investigation for binary Pb–In system are presented on Fig. 1.

From Fig. 1, one can see this subject investigated number of authors. Results are various. Diversity resulting with few phase diagrams of binary Pb–In system.

In Fig. 2, comparative presentation of obtained results and calculated phase diagram of Nabot and Ansara [16] is presented. Nabot and Ansara results show the best agreement with experimental results.

From Fig. 2, one can see existence of two monophase area separated by intermediate (αIn) phase. On the left side of a diagram there is In based phase and on the right side Pb based solid solution. Also, presence of two peritectical reactions is evident. The first peritectical reaction occurs at 158°C, with equilibrium concentrations of 9.4 and 13.24 at% Pb (peritectical concentration 9.6 at% Pb). The second peritectical reaction takes place at 172.7°C with equilibrium concentrations of 18.7 and 28.75 at% Pb (peritectical concentration 25.3 at% Pb). Cited values for concentrations were deter-

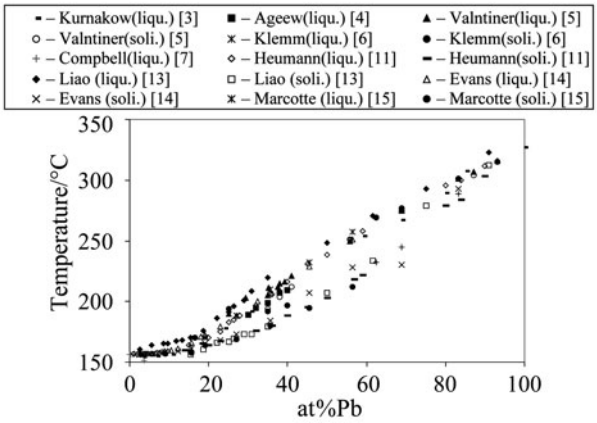

Fig. 1 Liquidus and solidus temperatures of binary Pb–In system

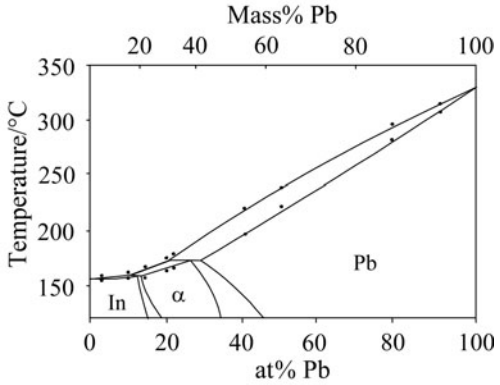

Fig. 2 The phase diagram of Pb–In system, (lines – Nabot and Ansara [16], dark points – this work)

mined by Nabot and Ansara [16]. Good agreement between experimental results and literature data of Nabot and Ansara [16] could be seen also in Fig. 2.

Crystallo – structural analysis

Crystallographic investigation was done at room temperature with X-ray diffractometry. Results are presented in Table 1.

Table 1 presents the results of crystalographic investigations done by X-ray diffractometry at room temperature. Based on that analysis, following could be concluded. Solid solution based on lead has FCC lattice. Crystal structure of lead is very well known line teseral with most dense packing. Lattice parameters are: a=4.9502 Å and V=121.33 Å^3 (JCPDS4-686, T=25°C). Crystal structure of In solution is FCT, I4/mmm. Lattice parameters are: a=4.5978 Å, c/a=1.0758 and V=52.3 Å^3 (JCPDS5 – 642, T=25°C). Intermediate (αIn) phase also is FCT with relation of c/a<1.

Table 1 Results of crystal phase investigation of binary Pb–In system

Sample	Structure type	Lattice parameters			
		a/nm	*c*/nm	*c*/*a*	*V*/Å^3
U1	In	0.46096	0.4992	1.0829	53.03
U2	In	0.46265	0.5007	1.0822	53.59
U4	InPb	0.48900	0.4541	0.9286	109.50
U5	InPb	0.48990	0.4530	0.9246	109.00
U6	Pb	0.48310	–	–	112.27
U7	Pb	0.48549	–	–	114.43

Dependence of lattice parameter *a* on composition is presented on Fig. 3.

It could be observed that *a* parameter slowely increases to concentration of the lead about 12 at% Pb. After that, the parameter *a* abruptly increases. In the concentration range up to below 30 at% Pb, the tendency of slower increase was obtained. At about 30 at% Pb there is larger difference in parameter *a* from 30 to 100 at% Pb, and parameter *a* slowly, but continuously increases.

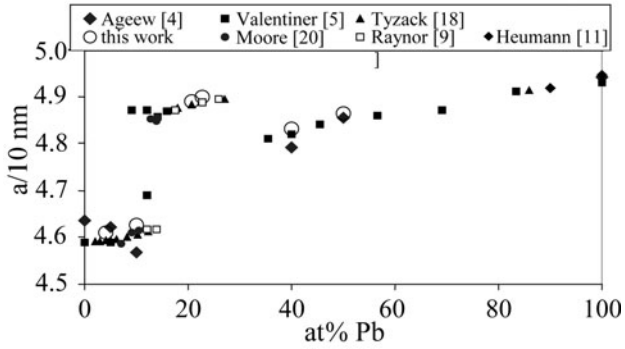

Fig. 3 Dependence of lattice parameter on composition

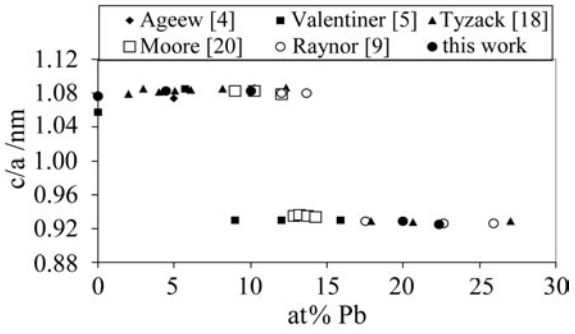

Fig. 4 Dependence of *c*/*a* ratio on composition

Mentioned deviation in *a* lattice parameter is a proof for existing phase boundaries. So, one can conclude about existence of three phases in the diagram. Additional proof for this is a dependence of ratio *c*/*a* on composition (at% Pb), (Fig. 4). For the first area, ratio *c*/*a*>1 and for second (intermediate phase αIn) *c*/*a*<1.

Microstructural analysis

In this part of the work, microstructural analysis of binary Pb–In system obtained by the SEM-EDX is presented. Three samples U1, U5 and U7 were analysed. The samples were chosen from each of the three noticed phases. Sample U1 solid solution with composition 95.53 at% In and 4.47 at% Pb. Microstructure of this sample as well as distribution maps are presented in Fig. 5a.

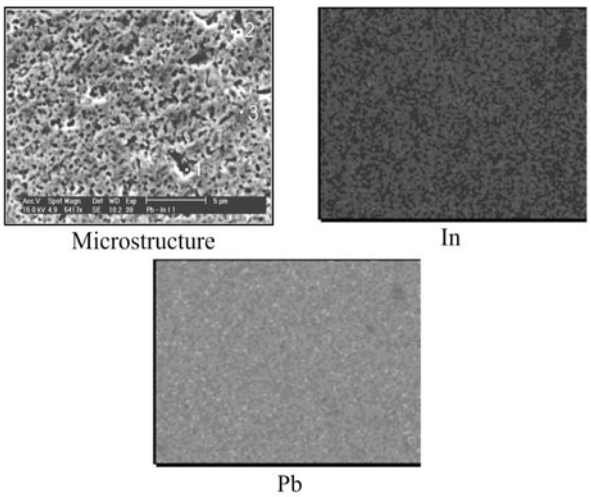

Fig. 5a Microstructure of binary Pb–In system and element distribution maps-sample U1

Marked points and microstructure were analysed, and results are given in Table 2a.

Table 2a Composition of points in Fig. 5a

Component	Point 1/%	Point 2/%	Point 3/%
Pb	78.25	30.11	24.7
In	21.75	69.89	75.3

Concentration of lead is highest in point 1, while at the same time, concentration of In is minimal. At the point 3, situation is opposite.

Sample U5 represents intermediate phase αIn, and contains 22.32 at% Pb and 77.68 at% In. As in previous case, three points were chosen for the analysis from microstructure surface (Fig. 5b). Results are given in Table 2b.

Results for U5 sample show difference in composition and structure in the intermediate phase. Parts which remind on dendrite base of others (Fig. 5b) are poor in comparison with sample composition.

Table 2b Composition of points in Fig. 5b

Component	Point 1/%	Point 2/%	Point 3/%
Pb	52.65	56.22	8.97
In	47.35	43.78	91.03

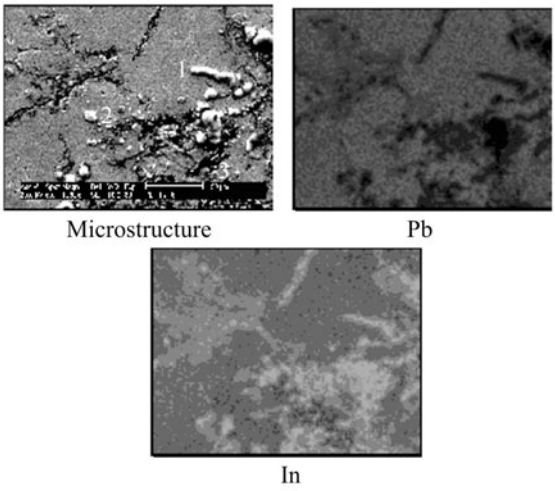

Fig. 5b Microstructure of binary Pb–In system and element distribution maps-sample U5

Composition of the sample is 50 at% Pb and 50 at% In and the sample U7 represents area rich on Pb. The same procedure as for previous samples analysis was used for this sample. These results are presented in Fig. 5c, while results for marked points in a microstructure are given in Table 2c.

Table 2c Composition of points in Fig. 5c

Component	Point 1/%	Point 2/%	Point 3/%
Pb	53.89	73.246	50.61
In	46.11	26.754	49.39

The highest composition of lead observed at point 2, where in the same time concentration of In is minimal. For other two points, content of lead and In is almost the same– near to 50 at% In. In both cases content of lead is higher.

In all analysed samples dark phase in microstructure contain higher concentration of In. For sample U1 microstructure, it is easy to observe whitegray structural base which

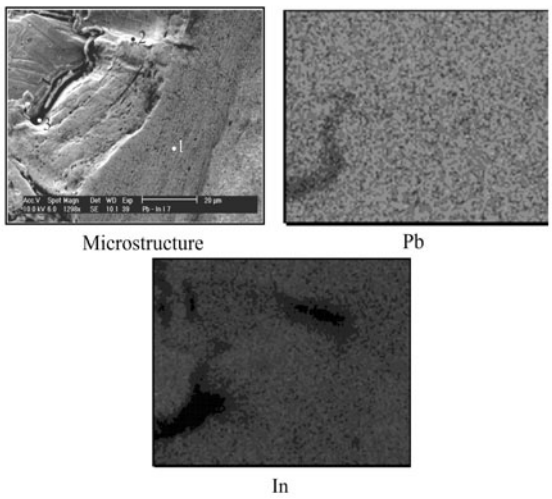

Fig. 5c Microstructure of binary Pb–In system and element distribution maps-sample U7

represent solid In based solution. Composition of points 2 and 3 is almost the same and slight difference in colour is due to the chemical segregation of crystals. Through whole surface dark structural area (which has to be crystal segregations) can be observed.

For sample U5 microstructure, one can observe bright spherical parts, which probably represents crystal. Dark crystal base is intermediate αIn phase form by peritectical reaction.

The presence of gray structural base and crystal segregation is evident for the microstructure of sample U7.

Conclusions

According to experimental results presented in this work, it can be concluded that binary phase diagram Pb–In consists three areas: solid solution based on In with FCT structure, solid solution based on Pb with FCC structure and intermediate phase αIn with structure FCT.

Concentrations at which great changes in lattice parameters *a* and in *c/a* ratios occur are in agreement with phase boundaries. The results of microstructural analysis confirmed that observation.

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