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Expansion of solidified lead bismuth eutectic

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Abstract

Lead bismuth eutectic (LBE) has been proposed both as spallation target and as coolant in a future accelerator driven system (ADS). Therefore this alloy should be fully characterised and its physical properties should be completely known before use. Experiments on the volumetric expansion of LBE were performed by variation of cooling rates, holding times and different starting temperatures of the melt. X-ray diffraction and optical metallurgical examination on LBE has been carried out in order to clarify the reasons for the volumetric expansion of LBE. Additionally thermal expansion of LBE_{solid} was revealed. The results achieved will be discussed and at the end a model assumption will be given trying to explain the processes taking place to an ideal eutectic mixture.

1. Introduction

There are many good properties to foresee LBE (lead bismuth eutectic) both as spallation target and as coolant in a future accelerator driven system (ADS) obverse to other liquid metals or alloys [1,2]. A relatively low melting point ($T_m = 123.5$ °C) helps avoid quite easily freezing of LBE under operation. The low vapour pressure and the non-existence of heavy reactions with oxygen or nitrogen make the handling of LBE quite uncomplicated. The good properties as spallation neutron target material have also to be mentioned: yield of about 28 n per 1 GeV proton is very high, LBE has an extremely small neutron absorption cross section and the moderation of neutrons is very little. As disadvantages should be mentioned the possible interactions between steels and LBE, which might lead to liquid metal corrosion or liquid metal embrittlement (LME). Generation of Po-isotopes and volatile elements during irradiation could display a problem under operation. A physical phenomenon is the expansion of solidified LBE after freezing which can arise high stresses on the walls of a vessel [3–5]. This phenomenon imposed severe constraints in the operation of experimental facilities, corrosion layers and target. Therefore the reasons for this behaviour of LBE should be enlightened and the mechanism responsible for it should be clarified and understandable.

2. Empirical observations and basic data

Numerous cases are reported in which volumetric expansion of LBE after freezing has been observed [3–5]. The expansion curve in Fig. 1 is given as an example. It is obvious that with increasing time solidified LBE expands and this aging process lasted up to one year. Although this phenomenon is known, the mechanism, however, is not quite well understood.

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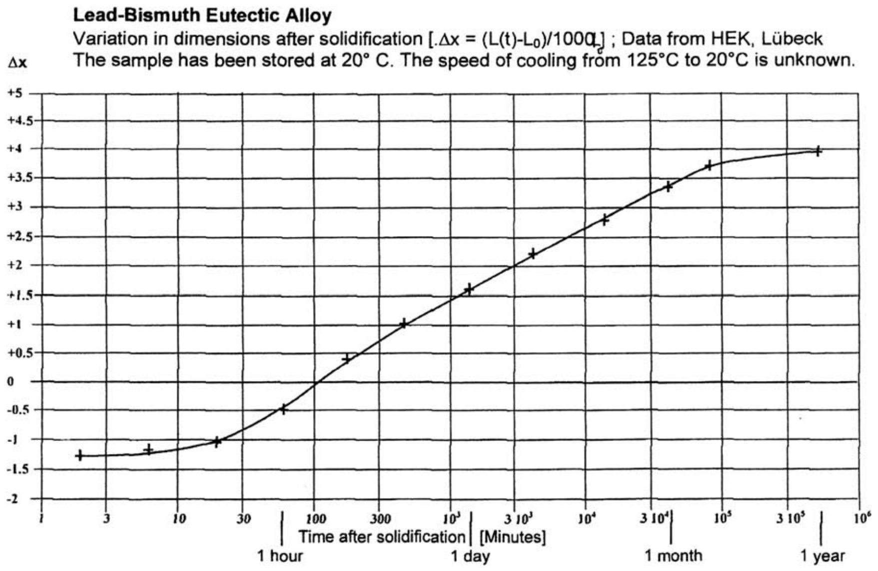


Fig. 1. Linear expansion of LBE after solidification and holding at RT [3].

Table 1
Densities of Pb, Bi and LBE given at different temperatures

T [°C]		130	200	300	330	400	450	500	600	Ref.
D [g/cm^3]	LBE	10.57	10.46	10.16		10.19			9.91	[6]
		10.570	10.486	10.364		10.242		10.120	10.00	[5]
		10.55	10.46	10.33		10.21	10.150	10.08	9.96	[7]
	Bi						9.854			[7]
				10.03		9.91			9.66	[8]
	Pb				10.67	10.58	10.520	10.46	10.34	[7]

A closer look to the behaviour of the liquid alloy LBE and the melts of lead and bismuth show positive thermal expansion behaviour; i.e. they expand with increasing temperature and no abnormality exists. The changes in density with temperature are given in Table 1.

From the data given in Table 1, the volumetric expansion coefficients of the liquid melts and alloy can be calculated:

$$\text{Pb:} \quad \alpha_V = 1.1605 \times 10^{-4}\ \text{K}^{-1},$$

$$\text{Bi:} \quad \alpha_V = 1.2767 \times 10^{-4}\ \text{K}^{-1},$$

$$\text{LBE:} \quad \alpha_V = 1.2550 \times 10^{-4}\ \text{K}^{-1}.$$

The volumetric expansion coefficient of LBE is between the values calculated for the pure melts of lead and bismuth.

3. Experimental

Eutectic Pb–55.5Bi (44.8 wt% Pb and 55.2 wt% Bi) alloy LBE used for the experiments was supplied by Impag AG (Switzerland) having the following impurities (given in ppm): Ag 11.4, Fe 0.78, Ni 0.42, Sn 13.3, Cd 2.89, Al 0.3, Cu 9.8, Zn 0.2.

Several analytical methods were used to examine solidified LBE in aged and non-aged status in order to learn about the origin and cause responsible for the expansion of LBE after freezing. Metallurgical examination was performed on polished LBE specimens cooled down with different velocities: air cooled and 0.1 °C/min to see whether this has a visible influence on the micro structure.

Several freezing experiments have been performed by variation of different parameters. The complete list is shown in Table 2. The treatment of the specimens was done under well-defined conditions in an oil thermostat which is able to control the temperature in the range of $\Delta \pm 0.1$ °C. LBE was filled into test tubes, so-called glass vials, with an inner diameter of 9 mm. In the fourth column named ‘time to break’ the number of days are given until the test tube was broken. In the case of more than one specimen prepared under the same conditions the average value is given in the duration column.

Table 2
Summary of the freezing experiments carried out

No.	Mass [g]	Treatment	Time to break [d]	Comment
1	18.8	150 °C/30 min – oil/RT	3	3 samples: 2, 2, 6 (15.5 g)
2	18.8	150 °C/30 min – air/RT	5	5 samples: 6, 6, 6, 6, 2 (16.5 g)
3	18.8	150 °C/30 min – 1 °C/min – RT	7	1 sample
4	18.8	150 °C/30 min – 0.1 °C/min – RT	18	1 sample
5	18.8	200 °C/30 min – air/RT	1	1 sample
6	18.8	250 °C/30 min – air/RT	3	1 sample
7	37.6	150 °C/30 min – air/RT	8	1 sample
8	18.8	150 °C/30 min – 127 °C/30′ – RT	6	2 samples: 6, 6
9	18.8	150 °C/30 min – 127 °C/30′ – 1 °C/min – RT	9	1 sample
10	18.8	150 °C/30 min – 127 °C/30′ – 0.1 °C/min – RT	33	1 sample
11	18.8	150 °C/30 min – 127 °C/30′ – 0.02 °C/min – RT	158	2 samples (1 for examination)
12	18.8	150 °C/30 min – 120 °C/60′ – RT	14	2 samples: 14, 15
13	18.8	150 °C/30 min – 100 °C/60′ – RT	7	1 sample
14	18.8	150 °C/30 min – 80 °C/60′ – RT	7	1 sample
15	18.8	150 °C/30 min – 60 °C/60′ – RT	12	1 sample
16	16.5	150 °C/30 min – 45/24 h/ – RT	3	1 sample
17	18.8	150 °C/30 min – 100 °C/300′ – RT	10	1 sample

Dilatometer measurements were done in the range of 0–94 °C. The point of origin was set for $\Delta L/L_0$ to 0 at 20 °C before each run begun. Altogether three experiments have been performed by using always the same LBE specimen. Hence only the first measurement was carried out on an aged specimen, second and third measurements have been performed on LBE which might change during the heat treatment of the first experiment.

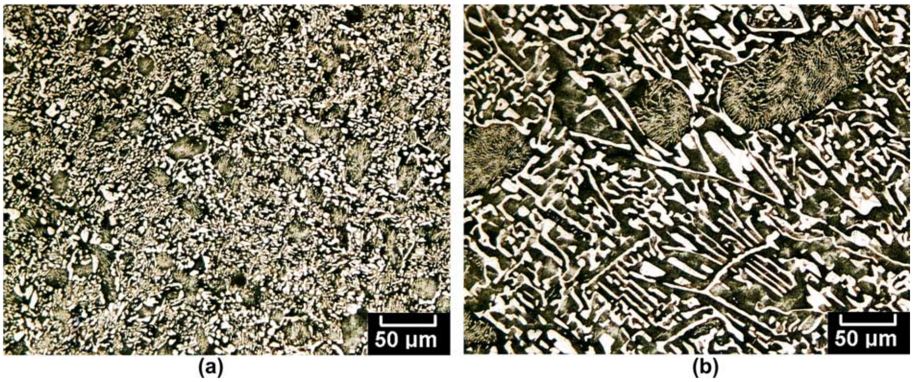
In total two DSC (differential scanning calorimetry) experiments have been performed running up to 140 °C by using twice the same specimen. In the first test LBE specimen was already aged, the heating up over the melting point has again created a non-aged specimen.

XRD-measurements have been performed on solidified LBE after fast and slow cooling of the melt down to room temperature. To investigate the time dependent change in the structure of LBE nine spectra were recorded of each specimen within 70 h.

4. Results and discussion

4.1. Metallurgical examination

The polished surfaces of solidified LBE specimens were examined after slow (0.1 °C/min) and fast freezing (in air) of the melt. In both specimens the characteristic eutectic fishbone structure is visible consisting of the γ-phase (Bi) and β-phase (Pb_7Bi_3). Additionally some micro segregation is present. The micro structure obtained on the slowly cooled LBE specimen is coarser compared with the fast cooled LBE which has a very fine structure (see Fig. 2(a) and (b)). The inspection of each



(a) (b)

Fig. 2. Micrograph of polished LBE specimens (a) cooling down in air and (b) controlled cooling (0.1 °C/min). The white areas correspond to γ-phase, the dark to β-phase and the micro segregation is characterised by a fine structured zones.

specimen over a longer period did not reveal any visible variation in the structure (position was marked by a sign revealed by micro hardness). Anyhow it cannot be excluded that changes in the micro structure occurs during expansion but this is probably in the atomic scale and hence it cannot be observed by optical microscopy.

4.2. Freezing experiments

In Fig. 3 a broken glass vial filled with LBE is shown. The crack is easily to observe and occurred by expansion of LBE during aging process, i.e. transformation into a structure with a lower density. The values of Table 2 are put into a graph (Fig. 4). The experiments indicate that the time to failure increases with decreasing cooling rate and with lower start temperatures. Approaching the equilibrium conditions with lower cooling rates optimises the transformation and creep at higher temperatures. As expected, the cooling rate has a strong effect on the microstructure. It seems, however, that the alloy is not a pure eutectic or has suffered from segregation. The globular phase – micro segregation – is may be primary hypoeutectic β-precipitates.

Fig. 3. A crack in a broken glass tube demonstrates the expansion of LBE during aging.

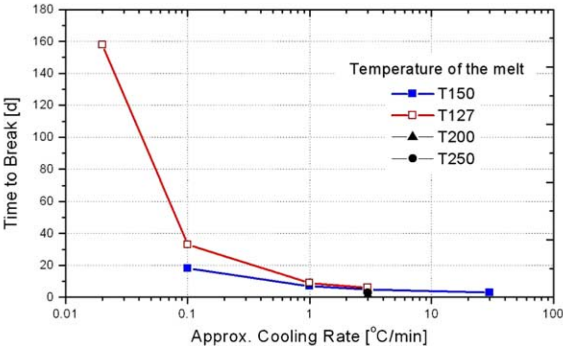


Fig. 4. Time to failure of glass vials as a function of cooling rate.

4.3. Dilatometer measurements

In total three measurements were performed by using always the same sample. It is obvious that the curve of the first measurement has a different shape than the curves revealed in the second and third run which are nearly congruent (Fig. 5). The redrawing of the curves by avoiding the calibration of $\Delta L/L_0$ to 0 at 20 °C for the second run show that LBE had undergone a shrinkage (compare the shift of the curves of run 1 and 2 in Fig. 6).

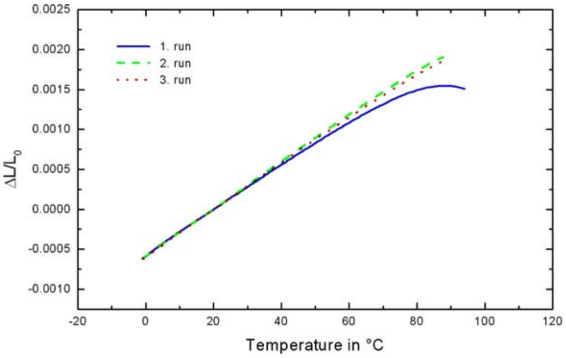


Fig. 5. Results of the three dilatometer measurements occurred on LBE.

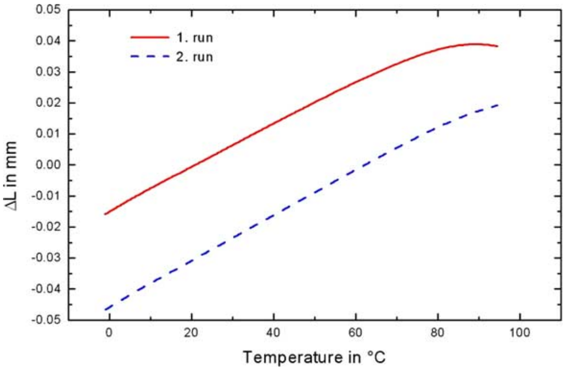


Fig. 6. During the first run LBE specimens underwent shrinkage.

The basic material was aged LBE, i.e. the melting and freezing was done about four months before dilatometer measurements were performed. Comparing this with the expansion behaviour of LBE (see Fig. 1), expansion process should be nearly completed. The heat treatment of LBE during the first dilatometer measurement might transform the aged material again into 'fresh, virgin' material although the specimen was only heated up to 94 °C which is approximately 31 °C below the melting point ($T = 125.5$ °C). It seems that LBE expands during aging and that the process can be reversed i.e. shrinking of LBE although it is not heated up to the melting point. Hence this process 'expansion–shrinkage' seems to be a reversible reaction.

The densities of liquid and solid (Table 1) Pb, Bi and LBE are put together in Fig. 7. Beside the three reference data for solid LBE published in the literature, experimental data are included for solid LBE revealed by dilatometer measurements.

Density change of LBE, Pb and Bi with temperature and density shift by transforming into another state (solid–liquid) is clearly visible.

Lead has a higher density in solid state than in liquid whereas bismuth has a lower density in solid state than in liquid. This means that pure bismuth expands during the transition from the solid into the liquid state whereas pure lead shrinks during phase transition solid–liquid.

The density revealed by our dilatometer measurement on aged LBE is lower (i.e. larger volume) compared to 'fresh, virgin' LBE, which has a higher density (i.e. minor volume). This explains the discrepancy of the density values published previously [6,7,9]. The values present in [9] gives a much higher density than the two nearly identical results presented in [6,7], because LBE chosen for these experiments had different micro structure (aged and virgin material). In the case of LBE, however, it is important to know the exact history of the material used for testing because the density is dependent on the microstructure which alters by time. Our experimental data are in good agreement with the three density values published earlier and density values of aged and virgin LBE are more or less on the same curve.

Aged LBE shows the same behaviour like pure Bi: lower density in solid than in liquid state; whereas fresh, virgin LBE acts like Pb: higher density in solid than in the liquid state.

4.4. DSC measurements

The DSC cooling curves of measurement 1 and 2 obtained on LBE are congruent (Fig. 8(a) and (b)) because during the experiment the sample is heated up over the melting point ($T_{\max} = 139$ °C) and therefore LBE used to measure the signal during cooling had the same history (melting and freezing under the same controlled conditions). Whereas a difference in the DSC curves revealed during heating is observable. The curve achieved during the first DSC measurement on aged LBE shows a single peak with a shoulder, hence LBE examined does not melt uniform but it seems that beside the eutectic compound another phase exists. The signal measured during the second heating procedure on LBE is also not fully symmetrically but the main peak shows only a slight asymmetry. In general one can say that during the aging process another phase is formed which

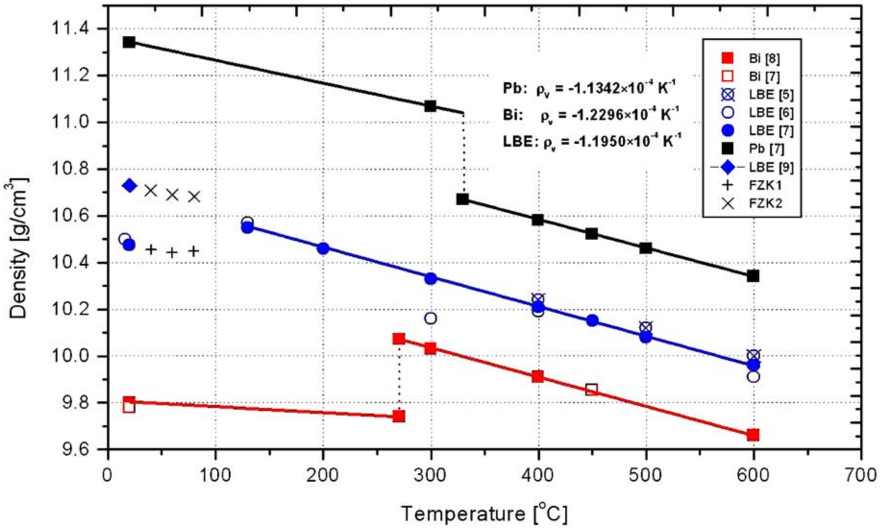


Fig. 7. Density change of LBE, Bi and Pb with temperature including our experimental data revealed by dilatometer measurements on solid LBE.

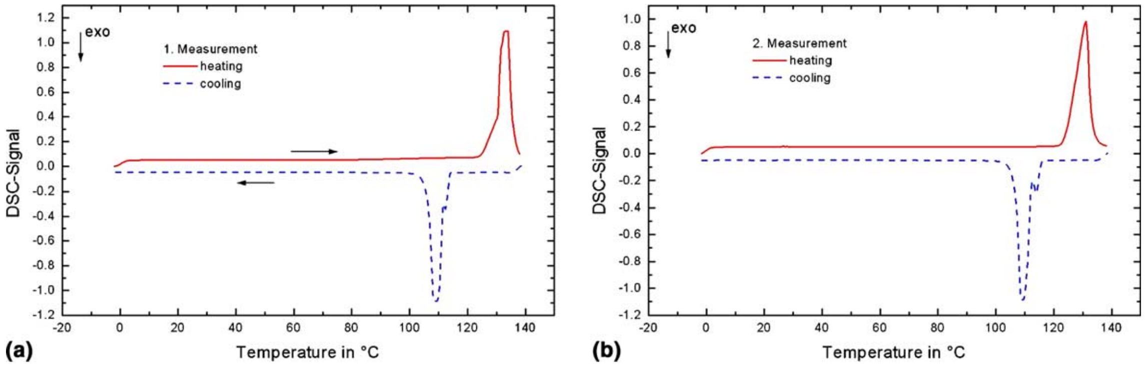


Fig. 8. Curves revealed by DSC measurements on (a) aged LBE and (b) 'virgin, just molten' LBE.

seems to be responsible for the expansion. During heating up of an aged LBE sample to about 100 °C or higher this process is retracted, hence it is a reversible, time and temperature dependent process.

4.5. XRD measurements

X-ray diffraction (XRD) can determine which crystallographic phases are present in a sample. Hence it seems to be a powerful tool to observe phase transformations. Two LBE specimens were examined (fast and slow cooled) by observing the temporal change of the spectra during 70 h. The results achieved on the two samples are the following: as expected the corresponding peaks of γ- and β-phases are present. There can be observed a drift to smaller lattice parameter which occurs quite fast after freezing. Such a drift indicates shrinkage and this is in agreement with the values plotted in Fig. 7 (increase of density of LBE by phase transition liquid–solid). In the case of fast cooled LBE specimen this drift was more pronounced than as it was observed on the slowly cooled down LBE specimen. At the end of the observation time (70 h) the last spectrum obtained on each sample (slow and fast cooled), however, are congruent concerning location and size of the peaks. Additionally it is obvious that the height of the peaks changed by the time: the γ-peaks assigned to the increased (i.e. the amount of this phase increases) and in parallel the peaks corresponding to the β-phase decreased. In Fig. 9 one single peak of the γ-phase was picked to demonstrate the drift and the gain in height of this peak by the time. It is clearly shown that the shift is more pronounced in the beginning of the observation (directly after freezing) while the increase in the height of the peak (i.e. formation of this phase) seems to start a bit later. All peaks could be assigned to γ- or β-phase except one which was coming up in the fast cooled LBE during 70 h. In the first spectrum this peak was not present at all and a classification to a certain phase is still missing. It should be mentioned that in the spectra revealed on Pb–40.0 wt% Bi this unknown peak was observed as well. In the near future some work will be done in order to clarify this point.

The observations made by X-ray on fast and slow cooled LBE are summarised here: at first a drift of the peaks has occurred which means the lattice parameter changed and showed shrinkage of LBE. By the time peaks of the γ-phase were growing and the peaks of the β-phase were decreasing.

5. Conclusions

XRD, dilatometer and DSC measurements have revealed all the same results: aging of solidified LBE (i.e. expansion by time) is a change of the proportion of β- and γ-phase to each other. This phenomenon takes place at the level of crystal grains in the atomic range and cannot be observed by metallurgical examination. Surprisingly the transformation of β-phase into the γ-phase at room temperature is a reversible process and an increase of temperature (about 94 °C seems to be sufficient) affects shrinking of before expanded (aged) LBE as can be shown by dilatometer measurement.

In the following a possible explanation for the expansion of solidified LBE is given: the eutectic reaction of $L \rightarrow \gamma + \beta$ was found to occur at $T = 123.5$ °C. In Fig. 10 the phase diagram of Pb–Bi is plotted [10]. γ-phase is a solid solution of Pb in Bi consisting of 99.6 wt% Bi with a small amount of Pb and β-phase is an intermetallic compound with 42 wt% Bi at 123.5 °C and 33.8% wt% Bi at 0 °C. We believe that during freezing β-phase with approximately 42 wt% of Bi is formed which is not stable at room temperature with that high concentration of Bi. If the cooling process it too fast (normal conditions), the partly transformation of β into γ-phase cannot occur immediately but it is taken place within a year (see Fig. 1). The reasons for the expansion can be explained as follows: β-phase Pb_7Bi_3 crystallises in hcp structure which has a theoretical volumetric density of

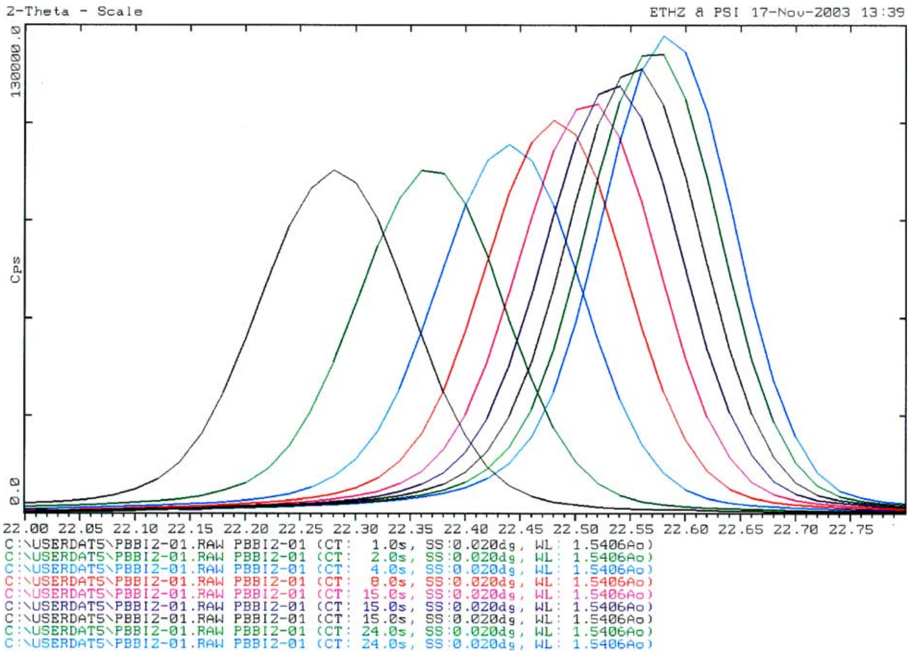


Fig. 9. Aging process observed on LBE starting directly after freezing with XRD during 70 h. Shift to lower lattice parameter and increase in height are achieved on Bi peak.

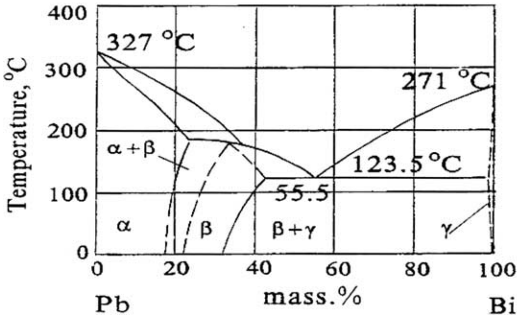


Fig. 10. Phase diagram of Pb and Bi.

74% and a density of 11.17 g/cm^3. Due to the fact that the atomic radius of Bi and Pb are not identical (Bi = 143 pm, Pb = 154 pm) this high volumetric density is surely not reached. Crystal structure of γ-phase Bi (0.4% Pb) is rhombohedral. The volumetric density of pure Bi is with 44.5% quite low compared to hcp. The density of Bi is 9.747 g/cm^3. If the close packed β-phase is now partly transformed into the γ-phase needing much more space, the result during aging of LBE is an expansion of the specimen. The reverse process happens during heating up of LBE and shrinkage can be measured: γ-phase is partly retransformed into β-phase until the saturation content of Bi at the particular temperature is reached. For example β-phase with 40 wt% of Bi will be formed at 100 °C. Due to elevated temperature the retransformation is much faster than the aging at room temperature.

The slow cooling processes (up to 0.02 °C/min; see Table 2) applied to liquid LBE shows that the partly transformation of β-phase with 42 wt% Bi started already during cooling and due to elevated temperature this process is more rapid than during room temperature. The processes shrinkage of LBE sample during phase transition liquid–solid (Fig. 7) and expansion of LBE during aging can therefore partly be compensate each other. But the aged LBE has a lower density than molten LBE and thus the volume needed is higher i.e. the glass vial still breaks just later than the fast cooled specimens.

The reasons for the retransformations (reversible process of phase transformation) are not fully understood up to now and further investigations and new considerations have to be taken into account.

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