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Post-melting anomaly of Pb–Bi alloys observed by internal friction technique

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Abstract

With the help of an improved internal friction method, it was found that a peak could appear, as the temperature increased, above the liquidus in each of the internal friction curves of Pb–Bi alloys. The features of this kind of peak are similar to those found during the solid–liquid transition in the same experiments, and in accordance with the characteristics from solid–solid transitions verified by previous investigators. The results suggest that structural changes take place to some extent in the molten alloys as a function of temperature, which have been confirmed by the corresponding calorific peak in a differential scanning calorimeter. This phenomenon might help in understanding the nature of molten alloys and their melting mechanism as well. In addition, the internal friction technique proved to be quite sensitive to liquid structures and effective for studying liquid materials.

1. Introduction

It is of great importance to understand the structural information from melts at a temperature not too far above the liquidus (T_L) for us to understand the nature of liquids and to help elucidate melting mechanisms. On the other hand, there is an unsolved engineering question that the structures and properties of many alloys are related to the thermal history of their original melts. It has been widely accepted that there is a uniform, long-range disordered structure present after matter melts, no matter whether it is a single- or multi-component system. As one probes the liquid state of matter more and more thoroughly, however, there seems to be a general argument that some kinds of residual microcrystals and other clusters still remain in the melts after the fusion of crystal materials [1, 2]. With the experimental results from scattering techniques it has been proposed that there are domains of both spherical close packing and layer lattices in the melts of Au, Ag, Pb, Tl, Bi and the alkali metals [3, 4]. For Sn, shoulders appear on the right-hand side of the first peak of the scattering curves after fusion, but vanish around 750 °C, implying some structural changes as a function of temperature [5]. In recent years,

more significantly, liquid–liquid (L–L) phase transitions have been proved, experimentally and theoretically, to occur in some one-component liquid materials, e.g. Cs, Bi, Ga, Si, Se, Ge, C, S, H₂O and SiO₂ [6–10], and even in the two-component system Y₂O₃–Al₂O₃ [11]. Conventionally speaking, liquid phase separations could occur in some binary component systems, which have been recorded all along in their phase diagrams [12]. For most ordinary binary alloys, however, liquid structural changes and L–L phase transitions have seldom been observed. Owing to the complexity and diversity of liquid states, new and more sensitive experimental techniques are in great demand for understanding liquid structures and their patterns of change [1, 13].

Internal friction, as a structurally sensitive technique, has been widely used for studying structures, crystal defects, phase transitions, atomic diffusion and physical properties in terms of solid matter [14–18]. Most recently, with the ‘double material specimen’ method, the internal friction behaviour on fusion and solidification of pure Al, Cu and Pb–Sn has been investigated, showing that internal friction is also sensitive to S–L and L–S transitions [19, 20]. No doubt, these works could widen the scope of study of the internal friction technique, although further more detailed work should be carried out so as to provide wider and more useful structural and other information related to liquid states. In this paper, we report a post-melting anomaly in Pb–Bi alloys observed by an improved internal friction method. A peak arises on each of the internal friction temperature (Q^{-1} – T) curves above T_L as the temperature is increased. The features of the peak are strongly suggestive of structural changes in the molten alloys, which has been verified by the corresponding calorific peak in DSC. This phenomenon is a novelty, because there is only a single liquid phase zone in the ordinary binary phase diagrams, such as Pb–Bi.

2. Experiment methods

We carried out the experiments with an inverted torsion pendulum apparatus. In order to obtain the patterns of internal friction change of samples both during and after melting, we used tubes specially manufactured out of a Cr–Ni stainless steel, which proved not to react with Pb and Bi under the conditions of the pertinent experiments (see the following section). The outer and inner diameter of the tubes are 0.90 and 0.65 mm, respectively, into which the molten samples, prepared with pure Pb (3N) and Bi (5N), were filled by a vacuum method, then sealed and solidified. The sealed sample with the outside tube was used as the whole test specimen. All hollow tubes were previously annealed at 900 °C for an hour so as to prevent the tube itself from undergoing phase transitions during the experiments. The internal friction values of the specimens were measured from room temperature up to several hundreds of degrees above the liquidus, at a heating rate of 3 °C min⁻¹, with constantly oscillating amplitude and respective torsion frequencies of 0.5, 2.0 and 4.0 Hz. The alloys tested were Pb–Bi30, Pb–Bi56.1 and Pb–Bi80 in weight per cent. For comparison, the hollow tube and the specimens with pure Pb and Bi were also tested.

3. Results and discussions

As shown in figure 1, the Q^{-1} – T curve of the hollow tube is smooth, indicating no occurrence of any phase change in the tube during internal friction measurements. The continuous rise of internal friction values obviously results from the so-called high temperature background [14]. For the specimen tubes filled with Pb and Bi, a peak arises in each of the Q^{-1} – T curves at about 328 and 272 °C, respectively, corresponding roughly to their melting points (see figure 2 [12]),

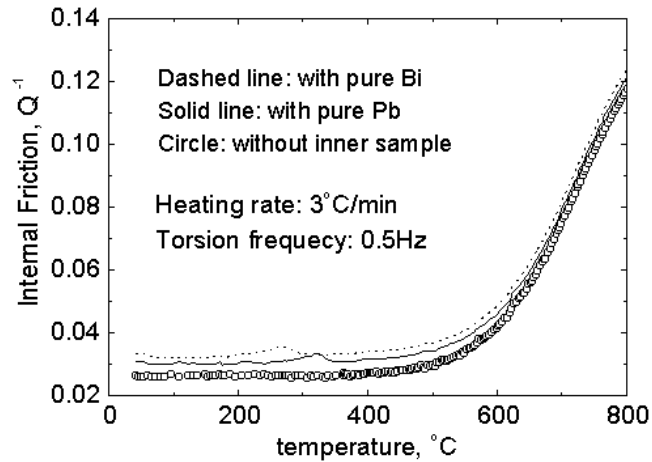


Figure 1. Internal friction patterns of specimen tubes filled with Pb and Bi, respectively, compared with that of the hollow tube.

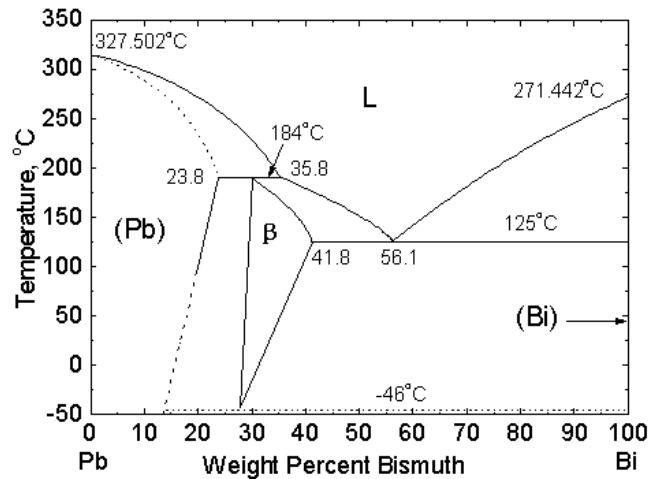


Figure 2. Phase diagram of the Pb–Bi alloy.

which suggests that this method is quite sensitive to structural changes. Above the melting points, the Q^{-1} – T pattern of the specimens with Pb or Bi is the same as that of the hollow tube, from which it can be inferred that neither of the elements reacts with the tube material under the experimental conditions.

Figure 3 shows the internal friction result (0.5 Hz) of the specimen filled with the sample Pb–Bi30, compared with that of the hollow tube. There are some peaks on the Q^{-1} – T curve of the specimen. In order to detect more clearly the internal friction pattern of the Pb–Bi30 samples themselves at different oscillating frequencies as the temperature is increased, we subtract the values of Q^{-1} of the hollow tube from those of the specimens with Pb–Bi30 and obtain the results at different frequencies, shown in figure 4.

According to the phase diagram for Pb–Bi (see figure 2), Pb–Bi30 contains only the β peritectic phase (solid solution) before the peritectic temperature ($T_P = 184^\circ\text{C}$) is reached. As the temperature is increased to T_P , the peritectic reaction $\beta \rightarrow \alpha(\text{Pb}) + \text{L}$ takes place. When the

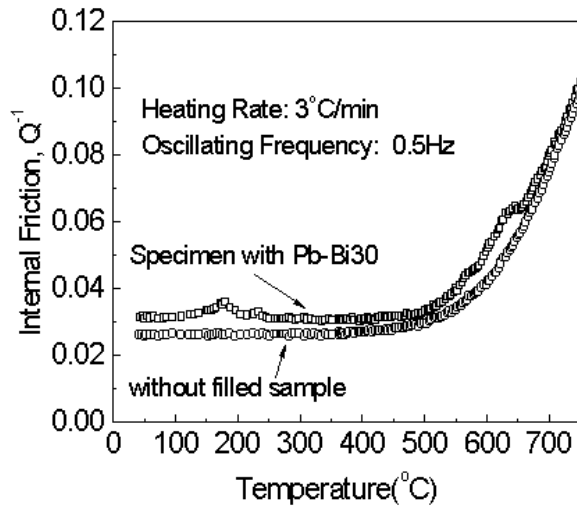


Figure 3. Internal friction patterns of specimens filled with the sample Pb-Bi30 wt%, compared with that from the hollow tube.

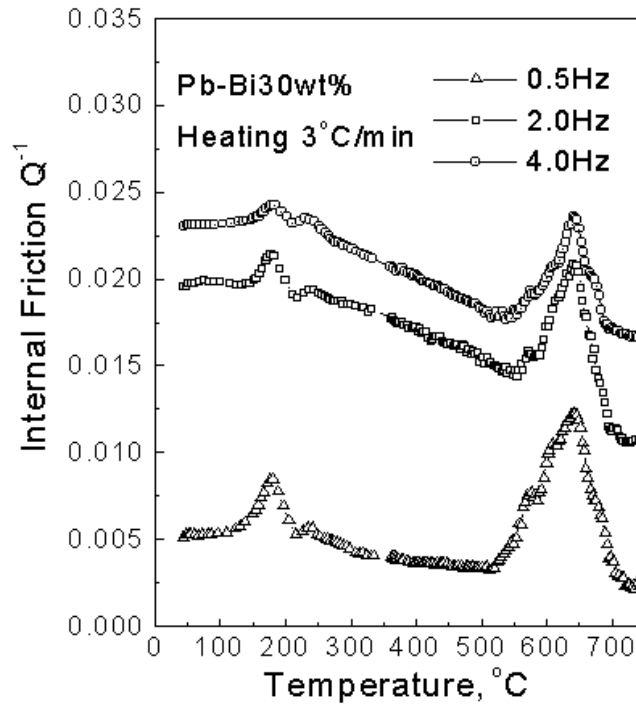


Figure 4. Internal friction patterns of Pb-Bi30 wt% at different oscillating frequencies, obtained by subtracting the values from the hollow tube from those of the specimens filled with the alloy.

temperature is over the liquidus ($T_L = 230^\circ\text{C}$), the alloy goes into a single liquid phase zone. Now let us make a detailed inspection of the internal friction pattern of the alloy Pb-Bi30 in figure 4. There are three peaks in each of the $Q^{-1}-T$ curves for all the frequencies. Evidently,

the first peak and the second minor one correspond to a peritectic reaction and the change $\alpha(\text{Pb}) + \text{L} \rightarrow \text{L}$, respectively, although the temperatures for the curves do not exactly represent those of the samples because the thermocouple could not contact the specimens directly during experiments. Just before the peritectic reaction, there is a continuous enhancement of the Q^{-1} value, suggesting a pre-melting phenomenon. For each of the first peaks, the position does not vary with the experimental frequencies, and the magnitude decreases as the frequency is increased. These features closely resemble those of the internal friction pattern during phase transitions in solids verified by previous investigators [11–15], which is understandable since the peritectic reaction is, after all, a phase transition. The mechanism of the internal friction peak features during solid phase changes was interpreted by the Belko and Delorme models [21, 22]. After complete fusion, the Q^{-1} values drop continuously in each of the curves, which could be attributed to the enlargement of the particle distance in the melt with elevated temperature. Interestingly, a large peak appears in each of the $Q^{-1}-T$ curves around about 645 °C, more than 400 °C above T_L , with two shoulders on the left-hand side of the peak. It should be stressed that the peak position is also independent of torsion frequencies, and its magnitude declines as the frequency increases, namely the characteristics of the third peak are again in good agreement with those during solid phase transformations. Based on the results of the specimens with pure Pb and Bi, the third peak could not result from the reaction between the alloy and the tube and there is no possibility of oxidation either, because the samples are sealed in the tubes. Therefore it is reasonable to infer that the characteristics of the third peak manifest some structural changes occur in the Pb–Bi30 melt. This phenomenon is anomalous since there is no phase line above T_L in the Pb–Bi phase diagram.

The internal friction patterns of Pb–Bi30 could be easily repeated in other Pb–Bi alloys with different compositions, with various peak positions depending on the content of Bi. For example (see figure 5), the correlative peak is around 610 °C for the melt Pb–Bi80, while for Pb–Bi56.1 (eutectic composition), the peak seems to consist of two peaks, with the maximum at 598 °C. Intriguingly enough, in some other alloys (Pb–Sn and In–Sn, for example), the $Q^{-1}-T$ peak also appears at a temperature much higher than T_L with the same features as mentioned above for Pb–Bi melts, although there are some specific differences in peak positions and shapes for different alloy systems. The detailed description of the results for other alloy systems will be published elsewhere.

In order to verify the possibility that some structural changes happen in Pb–Bi melts, we performed DSC experiments with a NETSCH DSC404. The Pb–Bi samples (50 mg) were held in Al_2O_3 ceramic crucibles, shielded by highly pure argon during the DSC measurements, and the heating rate was 6 °C min^{-1} . The DSC result from the sample Pb–Bi30 is shown in figure 6. Notice that an exothermic peak appears at about 660 °C, and afterwards the specific heat (C_p) increases with temperature. The position of this calorific peak corresponds roughly to that of the third $Q^{-1}-T$ peak although there is a difference of about 15° due to the higher heating rate in DSC. This fact excludes once more the possibility of a reaction between Pb–Bi melts and the tube material in internal friction experiments. The characteristics of the $Q^{-1}-T$ peak of Pb–Bi melts, together with the calorific effect in DSC, reveals that some changes in microstructure and properties could happen in the molten alloys as a function of temperature. In fact, Q^{-1} and C_p are themselves important properties of liquids.

As for the structure of Pb–Bi molten alloys, we assume that various minor conglomerate structures still exist in the melts at a temperature not too far above T_L . As a matter of fact, the entropy of vaporization for most matter is many times larger than that of fusion [23], which means atomic bonds in crystals are only partly broken when matter melts. As can be seen from the Pb–Bi phase diagram, the solubility of Pb in Bi is almost zero in the solid state, i.e. there are pure Bi crystals in solid structures of Pb–Bi alloys when $T < T_L$. Although the atoms

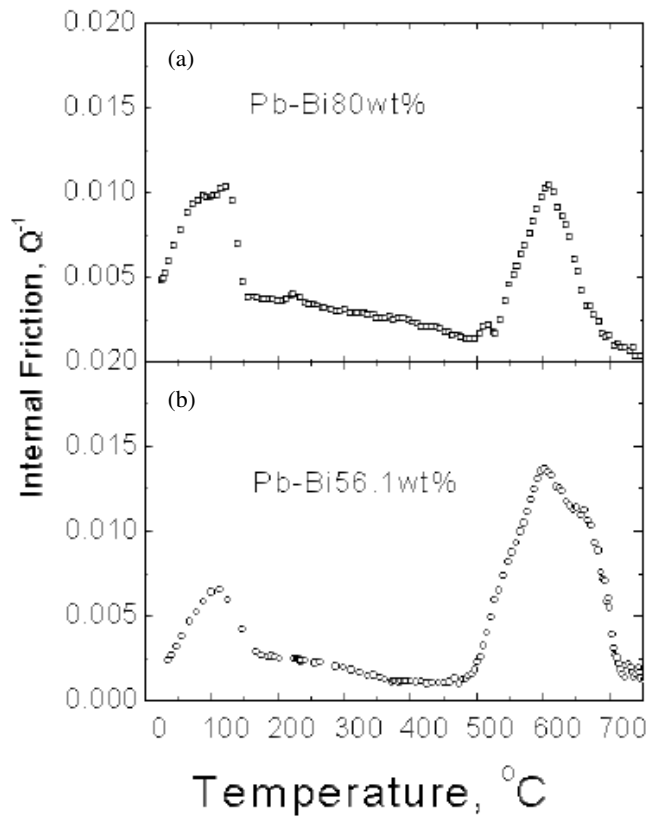


Figure 5. Internal friction patterns of Pb–Bi80 and Pb–Bi56.1 wt% at 0.5 Hz, obtained by subtracting the values from the hollow tube from those of the specimens filled with the alloys.

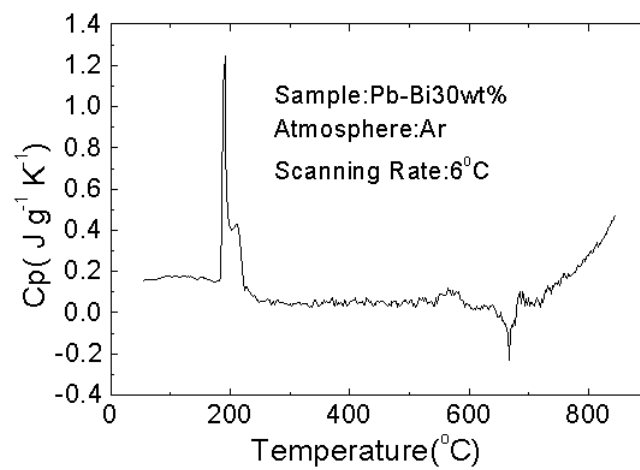


Figure 6. Heat capacity curve of Pb–Bi30 obtained with DSC.

of Pb and Bi are soluble in each other in the solid solution β phase, the solubility of Bi in α (Pb) drops after the peritectic reaction. It is likely, after fusion, that there are residual minor

crystals rich in either Bi or Pb in spite of the long-range disorder of the melts, i.e. the structure of Pb–Bi melts is heterogeneous when the temperature is not far above T_L . As the temperature is increased, the atoms within the residual crystals gain higher and higher energy. Once the critical temperature corresponding to the Q^{-1} – T peak is reached, the energy is high enough to overcome the energy barrier so that the atomic bonds of Pb–Pb and Bi–Bi in these residual minor crystals are broken continuously. At the same time, the Pb–Bi bond forms, and the molten alloy becomes a relatively homogeneous liquid. During the change in the structures, the area of the interfaces between the old and new structures increases at first and then declines, leading to an increase and then a reduction in Q^{-1} , so that a peak appears in each Q^{-1} – T curve around the critical temperature.

4. Conclusions

We have experimentally investigated the internal friction patterns of Pb–Bi alloys compared with pure Pb and Bi, from room temperature to hundreds of degrees above the liquidus. The peaks arising from solid–liquid transitions in these samples indicate the sensitivity of the improved method to structural changes. For Pb–Bi melts, the occurrence of the peak in the Q^{-1} – T curves above T_L implies that some change of structures and properties may take place as a function of temperature in these molten alloys, which has been confirmed by the calorific effect in DSC. This phenomenon, which we found in Pb–Bi melts also happens in some other binary component systems, is quite novel, because there is only a single liquid phase zone in the ordinary binary phase diagrams. We assume that the structure of the alloys is heterogeneous after melting, with residual minor crystals still existing. But when the critical temperature is reached, the residual conglomerates are broken and the relatively uniform structure appears. The present findings may help in understanding the nature of molten alloys and their melting mechanism as well. Moreover, the significance of the work also lies in that the internal friction technique proves to also be effective in studying liquids.

It should be pointed out that further work is needed to probe the concrete changes of structures and to find out the reasons for the details of the internal friction patterns of the alloys.

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