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Interactions in liquid bismuth-lead from sound velocity studies

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ABSTRACT

The sound velocity of alloys in the system Bi-Pb has been measured across a wide temperature range to high accuracy using a modified pulse-echo technique. The present work extends the measured temperature range and reduces the uncertainty in the measured values of the sound velocity of Bi-Pb system at high temperatures and in particular of liquid lead bismuth eutectic, which is being considered as a coolant in advanced nuclear systems. The composition range was sampled extensively and measurements were performed for the compositions Bi, $Bi_{20}Pb_{80}$, $Bi_{42}Pb_{58}$, $Bi_{48}Pb_{52}$, $Bi_{56}Pb_{44}$ (eutectic), $Bi_{64}Pb_{36}$, $Bi_{72}Pb_{28}$, $Bi_{86}Pb_{14}$ and Pb, from the liquidus to temperatures of about 1200 K. The temperature dependence of the sound velocity as a function of composition changes markedly in the vicinity of the eutectic composition. These data, together with other experimental inputs are employed to determine the pressure dependence of the interaction between the components in the Bi-Pb system. It was found that the interaction between the liquid solution's components becomes less attractive with increasing pressure. Finally, the interaction parameters obtained were incorporated into a thermodynamic model to study the pressure dependence of Bi-Pb system phase diagram. The position of the eutectic point in the composition-temperature plane is found to shift slowly with increasing pressure.

1. Introduction

Liquid metals continue to be a source of novel phenomena of both fundamental and applied interest [1–6]. The sound velocity of liquid metals is an important characteristic, affecting the adiabatic compressibility and the dynamic response of liquids, as well as providing a window into the high pressure behavior of the material system. Whereas relatively extensive studies have been performed on many pure liquid elements [7], only a few studies have been made of the physical properties of the multitude of alloy systems [8–15]. This paucity of studies lies in contrast to the relevance of the alloys in applications and the expanded phenomenology due to the additional degree of freedom in the composition. Of the binary alloy systems, arguably the simplest is the isomorphous system where the solid phase remains in the same structure at all compositions along the solidus. In a previous study, it was shown that for the isomorphous Bi-Sb system the sound velocity is a sensitive indicator of the deviation from ideality of the solution [16]. Furthermore, it was shown that the sound velocity is a significant discriminant of the pressure dependence of the solution interaction allowing prediction of the pressure dependence of the phase diagram.

In the present contribution, we focus on the Bi-Pb binary system which is an example of a eutectic system in which the solid phase changes structure with the composition along the solidus. The Bi-Pb eutectic system does not exhibit complete solubility of the two components at temperatures below the solidus, as depicted in Fig. 1 [17]. In the solid phase and at room temperature, lead and bismuth have different crystal structures: lead is fcc ($Fm\overline{3}m$) A1 and bismuth is rhombohedral ($R\overline{3}m$) A7 [18]. Therefore, the components do not have complete mutual solubility and the phase diagram of Bi-Pb system contains a eutectic point, see Fig. 1 [17] at which the binary liquid solution decomposes into two solid phases, typical of a repulsive interaction between the two components. The solid phases (Pb and ε) can be described as regular solutions, with a repulsive interaction between the components ($\Delta H_{mix} > 0$) and a positive interaction coefficient [18,19]. In the liquid phase there is an attractive interaction between the components ($\Delta H_{mix} < 0$) which is described beyond the regular solution model with a negative interaction coefficient [18,19].

Almost the entire database of thermo-physical properties of liquid Pb and lead-bismuth eutectic (LBE) is restricted to ambient pressure over a limited temperature range due to the difficulty in performing accurate experimental measurements on liquid metals at high temperatures and even more so at high pressures [20]. Several of these studies have identified anomalous temperature dependence in the liquid phase of the alloy in the regime of 900-1000 K which has been interpreted as an indication of structural rearrangement [21,22]. In particular, very limited measurements of the sound velocity of Bi-Pb alloy at the eutectic composition have been reported beyond ca. 600 K [20].

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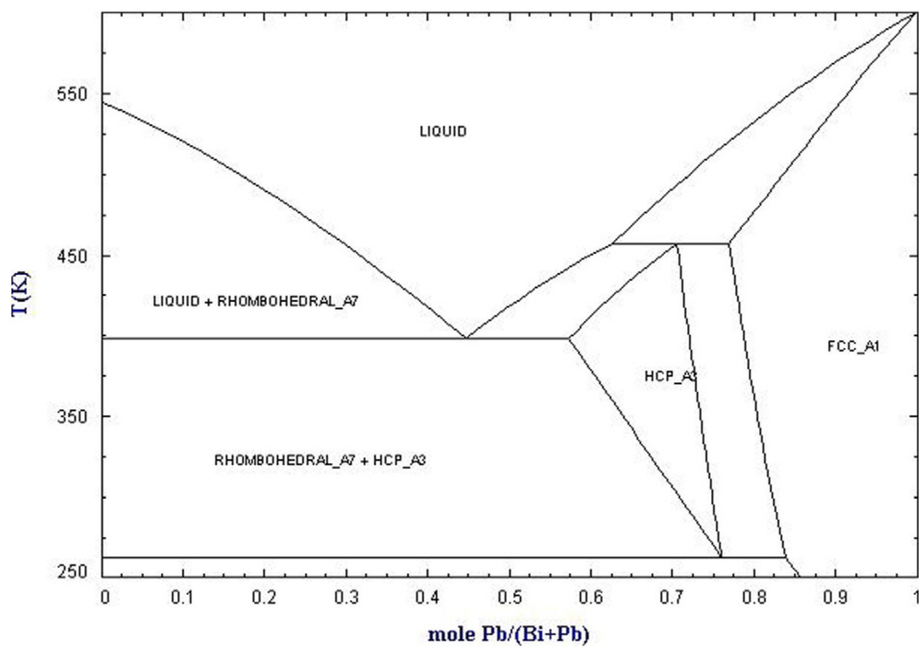

Fig. 1. Phase diagram of bismuth-lead from the SGTE database generated with FactSage [17].

In normal liquid metals, such as Pb, the sound velocity decreases with increasing temperature approximately linearly [23,24]. However, in Bi this dependence is monotonous, but variable [7,23]. Hence, the liquid Bi-Pb system is an attractive model to study the physical nature of eutectic systems.

In the present work we report on an extensive study of the sound velocity in the Bi-Pb system across a wide range of temperature and at multiple compositions. These highly accurate measurements are analysed and found to deviate from ideal solution behavior. The deviation from ideality is related within a thermodynamic model to the pressure dependence of the molar volume which controls the pressure dependence of the interactions parameters in a sub-regular solution model of Bi-Pb. The effect on the phase diagram and the location of the eutectic point in the Bi-Pb system as a function of pressure is discussed.

2. Experimental

Alloys of Bi-Pb at selected compositions were prepared from high purity bismuth and lead (5 N, 99.999%), by arc furnace casting in 10^{-5} Torr Argon atmosphere, at selected compositions of Pb_xBi_{1-x} ($x = 0, 0.14, 0.28, 0.36, 0.44, 0.52, 0.58, 0.80, 1$). To verify the composition, samples were weighed before and after the casting and cleaned with ethanol.

The velocity of sound was measured by the modified pulse-echo technique [23]. The experimental setup [16,23], consists of an alumina (Al_2O_3) crucible containing the liquid sample, positioned in a furnace. A 5 MHz piezoelectric transducer generates acoustic pulses which travel through a buffer rod (wave guide) into the liquid and are reflected back through the rod to the transducer. The velocity of the acoustic waves (C) is calculated from the ratio of the distance travelled by the wave to the measured time interval. In the modified pulse-echo technique [23] the sound velocity is obtained by displacing the buffer rod by a controlled distance, ΔX. This displacement leads to a change of $2\Delta X$ in the length of the path of the acoustic wave and consequently a change in the time interval, Δt, required for the wave to traverse the liquid. The sound velocity is thus obtained as $C = 2\Delta X/\Delta t$. Special care was taken to minimise any systematic or statistical errors in the acquisition of the data. The estimated error in determining the sound velocity is better than 0.3%. Details of the experimental procedure and analysis of the experimental errors were reported in [16].

3. Results

3.1. Temperature dependence of sound velocity in liquid Bi-Pb system

The temperature dependence of the ultrasonic sound velocity in liquid Bi and in the liquid alloys $Bi_{20}Pb_{80}$, $Bi_{42}Pb_{58}$, $Bi_{48}Pb_{52}$, $Bi_{56}Pb_{44}$ (LBE), $Bi_{64}Pb_{36}$, $Bi_{72}Pb_{28}$, $Bi_{86}Pb_{14}$ and liquid Pb was measured and the results are presented in Fig. 2. For each sample we obtained several sets of measurements which were found to agree within the experimental error.

The sound velocity in the alloy samples was measured from ca. 1150 K down to the liquidus temperature. The sound velocity near the liquidus ($C(T = T_m)$), the sound velocity temperature coefficient ($d\ln C/dT$) near the liquidus and the associated uncertainty ($\delta(d\ln C/dT)$) are presented in Table 1. It is seen that the sound velocity increases monotonously with composition from Bi to Pb.

The sound velocity near the melting points in liquid bismuth and liquid lead were found to be in excellent agreement with the previously measured values [16,23,26]. The sound velocity temperature coefficient in liquid Bi, represented by the slope $d\ln C/dT$ near the melting point, is

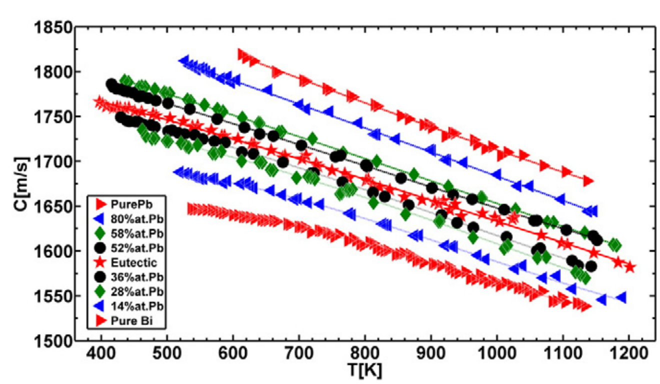

Fig. 2. Sound velocity in the liquid Bi-Pb system as a function of temperature at selected alloy compositions. Note that the symbols are larger than the error bars.