



Nanocalorimetry measurements of metastable states



John H. Perepezko*, Trent W. Glendenning, Jun-Qiang Wang

Department of Materials Science and Engineering, University of Wisconsin-Madison, 1509 University Avenue, Madison, WI 53706, USA

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ABSTRACT

Nanocalorimetry offers new capabilities to explore previously inaccessible domains of reaction kinetics due to the expanded heating and cooling rates compared to conventional calorimetry methods. With this capability it is now possible to explore ranges of alloy metastability and to examine rapid kinetic reactions such as melting and the competition between crystallization and glass formation. These capabilities are demonstrated for the melting of phases in Pb–Bi alloys, the melting and undercooling of Sn and glass formation in an organic compound *D*-mannitol.

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1. Introduction

Thermal analysis and calorimetry have proven to be of great value in the examination and determination of phase equilibria and thermodynamic properties. For the most part, due to the requirement to establish well defined conditions for measurement and the limitations from equipment design, the applications have been focused on stable equilibria and phases. With the advent of nanocalorimetry which offers unprecedented high programmed heating and cooling rates some of these limitations are removed so that a more extensive examination of phase reactions with rapid kinetics and metastable equilibria is now possible. While there are other advantages of nanocalorimetry such as the capability to conduct combinatorial experimental studies [1,2], the focus of this paper is on rapid reactions and metastability. The results of applying high cooling rates to promote large melt undercooling are well known, but the experimental opportunities offered by high heating rates are relatively unexplored. The capabilities will be illustrated with three examples: the determination of non-equilibrium melting behavior, the examination of undercooling and superheating effects on solidification and the measurement of critical cooling rate range for poor glass forming liquid. These examples support the unique capability of nanocalorimetry to provide new insight on the thermodynamics and kinetics of

reactions under conditions that were previously inaccessible to measurement.

2. Materials and methods

The Pb–Bi samples alloys were prepared from high purity (5 N) elements as either 20 μm droplets [3] or as thin (25 μm) slices from a melt spun ribbon. Prior to rapid heating in the Flash DSC (DSC, Mettler Toledo Flash DSC 1) the sample was annealed to yield a homogeneous solid solution in either the α or ϵ phase. The sample was loaded on the chip of the Flash DSC under an optical microscope. For the Flash DSC, the heating rate can be as fast as 40,000 K/s and the cooling rate can be as fast 10,000 K/s. The sample mass was estimated based upon the melting enthalpy.

Micro-sized Sn (5 N) droplets were prepared by the consumable-electrode direct current arc (CDCA) technique in various sizes [4,5]. Differential fast scanning calorimeter (DFSC) [5–8] based on thin film sensors was employed to investigate the relationship between undercooling and overheating. The nanocalorimeter sensors, XEN-39395 (Xensor Integrations, Netherlands), consist of an amorphous silicon-nitride membrane with a film-thermopile and a resistive film-heater placed at the center of the membrane.

A small *D*-mannitol particle with mass of about 55 ng was used in this measurement to determine the critical cooling rate and glass transition temperature. The sample was firstly heated up to 473 K, above the melting temperature, and held isothermally for 3 min to let the sample have a good contact with the chip. The melt sample was cooled to 223 K at various cooling rates ranging from

* Corresponding author. Tel.: +1 608 263 1678; fax: +1 608 262 8353.

E-mail address: perepezk@engr.wisc.edu (J.H. Perepezko).

50 K/s to 10,000 K/s and was subsequently heated at 100 K/s to measure the glass transition and crystallization behavior. The crystallization enthalpy upon heating was used to evaluate how much of the sample transforms into glass.

3. Non-equilibrium melting

Unlike pure metals, the melting of a binary alloy is accompanied by the redistribution of solute between the solid and liquid phases. In addition, while the superheating of pure metals is difficult to attain [9], it has been observed that relatively high levels of constitutional superheating can be achieved in bulk samples through the application of rapid heating rates [10]. At the same time, thermal analysis of fine powder samples (5–20 μm diameter) has proved to be a very effective method for analyzing metastable phase equilibria and evaluating possible reaction pathways leading to the formation of metastable phases during solidification [11]. The present investigation represents an extension of the droplet technique to investigate the path of morphological evolution during melting of solid solution alloys in the Pb–Bi system. The Pb–Bi system shown in Fig. 1 offers the opportunity to explore the melting behavior of the primary Pb solid solution, α phase as well as that for the adjacent intermediate ϵ phase which has a range of homogeneity. A systematic evaluation of the melting process and the onset of metastable effects were attained by analyzing the dependence of the melting signal on the applied heating rate. Some initial results are presented and a more complete analysis will be published elsewhere [12].

As background it is useful to consider the evolution of melting behavior of a solid solution with increasing heating rate. For a homogeneous solid solution of composition C_0 , as indicated in Fig. 2(a), upon reaching T_S , the solidus temperature, during heating the melting process would begin at the surface of the single crystal powders since there is essentially no barrier involved for liquid nucleus formation at the surface [13]. At a temperature just above T_S the droplets would consist of a solid core of composition C_0 surrounded by a thin liquid film of composition C_0/k (Fig. 2b). Further melting of the droplet would then involve growth of the liquid layer inward [14]. In order to observe melting under conditions approaching equilibrium (i.e. lever rule), the heating rate must be low enough to allow for complete (long range) partitioning of solute between the solid and liquid phases during heating. At a temperature, $T_S < T < T_L$, where T_L is the liquidus temperature, the liquid would then be of composition C_L , and the solid would have a uniform composition, C_S^* (Fig. 2c). As the heating rate is increased, however, the concomitant reduction in the time allowed for diffusion will result in the development of a composition gradient within the solid during melting and will

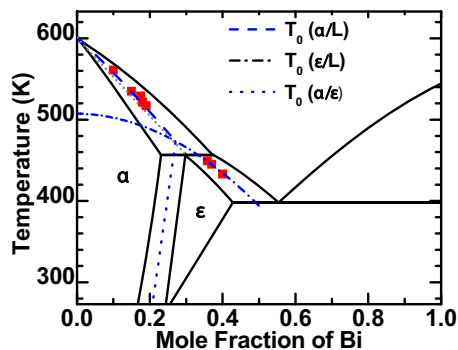


Fig. 1. The phase diagram of Pb–Bi binary alloys. Several calculated T_0 curves between the liquid, α , and ϵ phases are shown along with rapid heating melting onset measurements (square point).

eventually allow for the retention of a central core of β with its original composition C_0 at temperatures above its corresponding solidus. Assuming a smooth interface, complete diffusional mixing in the liquid, and that interfacial equilibrium is maintained, the droplet at a temperature, $T_S < T^* < T_L$ would then consist of liquid of composition C_L^* in equilibrium with solid of composition C_S^* at the interface. The solid adjacent to the interface would be depleted of solute, but some fraction of the solid core would be composed of α of composition C_0 (Fig. 2d). Although all of the solid present at a temperature T^* (including the solute depleted zone) would exhibit some level of constitutional superheating with respect to the corresponding solidus temperature, the maximum degree of superheating would occur within the retained C_0 solid (i.e. $T^* - T_S$). Further melting of this constitutionally superheated solid could occur at any temperature above T_S through internal nucleation of liquid ahead of the advancing L/S interface. It should be noted that a breakdown of the smooth interface can occur and still allow for the retention of C_0 solid within the center of a droplet.

The departure from near equilibrium melting behavior described above would occur more readily (with respect to the heating rate required) in systems which exhibit relatively sluggish solid state diffusion kinetics [15,16]. The diffusion coefficient, D of Bi in a $\text{Pb}_{90}\text{Bi}_{10}$ (at.%) alloy at the solidus temperature is about $2.6 \times 10^{-10} \text{ cm}^2/\text{s}$ [17]. A simple diffusion calculation shows that over the scales of time, t and distance, x relevant to these experiments, the diffusivity of Bi is not sufficient to allow for melting under equilibrium conditions (the diffusion distance, $X = (Dt)^{0.5}$ is approximately 1.3 μm for $t = 60 \text{ s}$). The rate of heat transfer within the α phase should, however, prevent the formation of temperature gradients within the droplets during heating [6].

Two phases with a common composition have the same Gibbs free energy at the T_0 temperature, and therefore, T_0 represents a limit to the partitionless transformation [18]. Once the sample reaches T_0 (the partitionless melting temperature) during heating, the growth of liquid present at the droplet surface or that nucleating within the C_0 solid would no longer require adjustment of the solid and liquid compositions at the interface, and the supersaturated α could then melt in a partitionless manner [19]. The result of a full calculation for the T_0 curve based upon Thermocalc [20] for both the α and the ϵ phases is shown in Fig. 1.

At a low heating rate of 1 K/s the observed melting onset in Fig. 3a corresponds to the solidus temperature for the $\text{Pb}_{90}\text{Bi}_{10}$ alloy. However, the melting event detected at heating rates above 1000 K/s was identical to the type of melting signal displayed by samples of pure Pb heated at comparable rates, as shown in Fig. 3b. In both cases the thermal signal exhibits a sharp onset which is characteristic of an invariant reaction. In addition, the measured temperatures of this reaction exhibit little, if any, heating rate dependence over the range investigated (Fig. 3c) and agree to within 1.5 K with the T_0 temperatures calculated from thermodynamic analysis. Based on the evidence presented above, the melting event detected at heating rates above 1000 K/s corresponds to the partitionless melting of C_0 solid retained metastable within the droplets and therefore can provide an experimental measurement of the alloy T_0 temperature.

From the determination of the T_0 curve for the melting of both the α and ϵ phases it is possible to determine also the location of the T_0 triple point that occurs at the intersection of the $T_0(\alpha/L)$ and $T_0(\epsilon/L)$. At the T_0 triple point (i.e., $T_0(\alpha/\epsilon/L)$) the free energies of the α , ϵ and liquid phases are equal. As shown in Fig. 1 the intersection of the $T_0(\alpha/L)$ and $T_0(\epsilon/L)$ is in good agreement with the calculated $T_0(\alpha/\epsilon)$ curve is also shown in Fig. 1. The continuation of the $T_0(\epsilon/L)$ curve to pure Pb corresponds to the lattice stability of Pb in the HCP structure. The comparison between the calculated and

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