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# Surface melting of nanometre-sized Pb particles embedded in an Al matrix studied by internal friction technique

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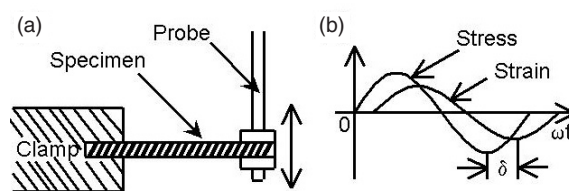
## Abstract

Nanometre-sized (hereafter n-) Pb particles embedded in an Al matrix were prepared by ball milling, and the surface melting behaviour was studied by the internal friction technique using a dynamic mechanical analyser. There is an internal friction peak appearing around Pb melting point and the height of the internal friction peak decreases with the increase of Pb particle size. Surface melting of n-Pb particles accounts for the internal friction peak. The study may throw light on the nature of surface melting in condensed matter physics. In addition, the present work makes a beneficial attempt at exploring internal friction as an experimental method for studying surface melting.

## 1. Introduction

The understanding of the crucial role of the surface of materials in melting process has been an open and widely studied question for almost a century, and it remains an unresolved problem [1]. Although there was no dearth of hypotheses, the first direct observation of surface melting was not described until 1985, by Frenken and co-workers [2]. Since then, surface melting has been studied widely [3–13]. In experiments, various methods, such as medium-energy ion scattering [3–5], low-energy electron diffraction [6], x-ray diffraction [7], calorimetric measurements [8] and electron microscopy [9, 10], have been used to study surface melting. All of the findings enrich the phenomenology of surface melting. However, in these studies the surface melting could not be distinguished clearly from the 'bulk' melting. In addition, most observational methods may introduce some unwanted effects on the melting behaviour. For instance, in electron microscopy measurements the sample temperature cannot be measured accurately because of the radiation effect of electron beams.

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**Figure 1.** Schematic diagram of (a) DMA setup in a bending mode with single cantilever geometry. (b) The phase angle  $\delta$  by which the responding strain lags behind the applied load stress.

Nanometre-sized particles embedded in a matrix can offer a unique system for studying surface melting, because particles in the nanometre size range can strongly enhance the surface-to-volume ratio and very strong signals can be given when the surface melts. Since Pb has a conveniently low melting point (327 °C) and is insoluble in Al, n-Pb particles in an Al matrix can be good samples for the investigation of surface melting.

Internal friction is a structure sensitive physical property and is a powerful technique for studying crystal structures, defects, atomic diffusion and phase transitions in solids [14–18]. Recently, investigations have shown that internal friction is also sensitive to solid–liquid transitions [19]. In this research, an internal friction technique is utilized to study the melting behaviour of n-Pb particles embedded in an Al matrix. The study shows that it is not ‘bulk’ melting, but surface melting of n-Pb particles, which causes the internal friction peak.

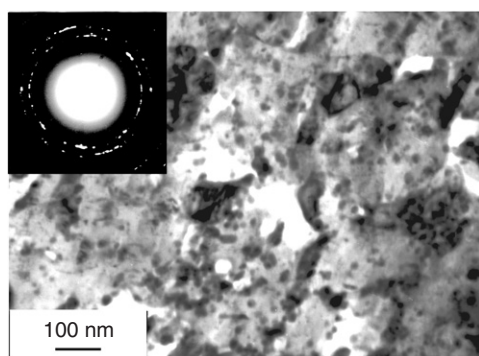
## 2. Experiment methods

In the experiment, n-Pb particles in an Al matrix were prepared by ball milling. Three grams of solid mixtures of 95 at.% pure Al (5N) and 5 at.% pure Pb (5N) were sealed in a steel vial with two large (8.3 g each) and four small (1 g each) hardened steel balls in a stationary nitrogen atmosphere, and milled for 12 h using a SPEX 8000 shaker mill. Then the milled powders were immediately consolidated by means of a specifically constructed die under a pressure of 0.9 Gpa at ambient temperature for 10 min. In this way, bar-shaped samples with dimensions of 3 mm × 1 mm × 30 mm were obtained. For comparison, pure Al samples were also prepared using the same procedure.

Internal friction was measured by means of dynamic mechanical analyser (DMA, Perkin–Elmer Pyris Diamond) in a bending mode with single cantilever geometry. During DMA testing, a periodic sinusoidal stress is applied to the sample through the probe, and the responding strain developed in the sample is measured; then the internal friction  $\tan \delta$  can be determined, where the angle  $\delta$  is the phase angle by which the responding strain lags behind the applied load stress (figure 1). All data acquisition and processing were completely controlled by a computer. In our experiment, four different oscillatory frequencies (0.5, 1, 5, 10 Hz) were chosen throughout the heating measurements with a heating rate of 2 °C min<sup>-1</sup>, and the force amplitude was 1 N. The Al–5 at.% Pb sample was repeatedly measured by DMA three times and then annealed at 500 °C for 2 h before the fourth DMA measurement. The morphologies of the samples were observed with transmission electron microscopy (TEM, JEOL-2010).

## 3. Results and discussions

The evaluation of the n-Pb particle size and its distribution was carried out with TEM. Figure 2 is a typical bright-field TEM image of the as-prepared Al–5 at.% Pb sample. It is found that



**Figure 2.** Bright-field TEM image of the typical as-prepared Al-5 at.% Pb samples. The inset is the corresponding SAED pattern.

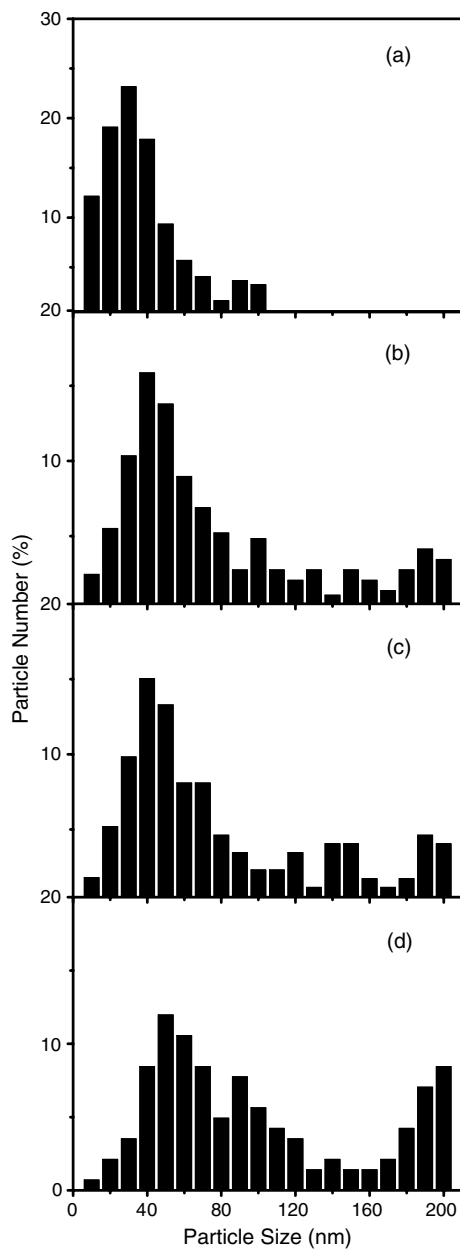
Pb particles are uniformly dispersed in the Al matrix. The statistics of size distribution was carried out with 246 particles for each kind of sample and the result is shown in figure 3. It can be seen that the particle size distribution of the Pb particles varies with the repeated heating measurements.

Figure 4 shows the DMA results for the pure Al sample. It is found that there is no peak. Figure 5 shows the internal friction–temperature  $\tan \delta$ – $T$  curves for the Al-5 at.% Pb samples. At every DMA heating measurement a single internal friction peak in the vicinity of the Pb melting temperature is observed, and the position of the internal friction peak does not change with measurement frequency, while the internal friction peak height drops with increasing frequency. The additional experiments also show the linear dependence of the peak height on the heating rates. These features are perfectly in accordance with those of the first order phase transformation in a solid [20]. For a fixed frequency, the height of the internal friction peaks, i.e.,  $H_n = \tan \delta_{\max} - \tan \delta_{\min}$ , varies with the number of times it is measured; here  $\tan \delta_{\min}$  refers to the minimum value of  $\tan \delta$  before the peaks,  $\tan \delta_{\max}$  the maximum value of the peaks, and  $n = 1, 2, 3, 4$  represents the measurement times. It can be seen that  $H_2$  is much less than  $H_1$  and is approximately equal to  $H_3$ , and  $H_4$  is the lowest (figure 6).

By comparing figure 5 with figure 4, it can be concluded that the internal friction peak must be related to the melting of the Pb particles. Two possible explanations for the origin of the internal friction peaks were proposed in [21]. One is that the internal friction is related to the surface melting, i.e., the melting/solidification process that occurs on the surface of Pb particles. The other is that the internal friction is caused by the aggregation process at which small liquid Pb droplets aggregate to large droplets after Pb particles melt in order to decrease the surface energy.

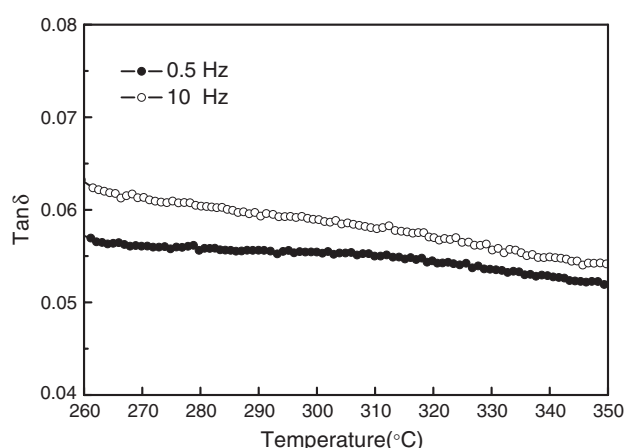
In order to investigate whether the internal friction is related to the aggregation process of liquid Pb droplets, the Al-5 at.% Pb sample was annealed at 500 °C for 2 h before the fourth DMA measurement. After being annealed, the n-Pb particles have grown larger and become stable [21]. So, there would be no aggregation of Pb in the following DMA heating measurement from room temperature to 350 °C. If the internal friction is related to the aggregation process, no internal friction peak should appear for this kind of sample. However, a peak with the height  $H_4$  still appears (figure 5(d)). Thus, it is inferred that the internal friction peak is not related to the aggregation process.

It has been established experimentally that melting begins preferentially at a surface [1]. By the technique of *in situ* heating in a transmission electron microscope it has been observed that the embedded particles melt first at the boundary between the particles and the matrix,



**Figure 3.** Size distribution of the n-Pb particles in the Al-5 at.% Pb sample: (a) as-prepared, i.e., before the first DMA measurement; (b) before the second DMA measurement; (c) before the third DMA measurement; (d) after annealed at 500 °C for 2 h, i.e., before the fourth DMA measurement.

such as for Sn-SiO<sub>2</sub>, Ga-SiO<sub>x</sub>, Pb-SiO<sub>2</sub> [9], In-Al [22], In-Fe [23], and Pb-Al [24] systems. We think that the internal friction is caused by the surface melting in our experiment. With the repeated DMA heating measuring process, the only difference in the Al-5 at.% Pb samples is the difference in particle size. It is the surface area change of the n-Pb particles that results in the change of the internal friction peak height.

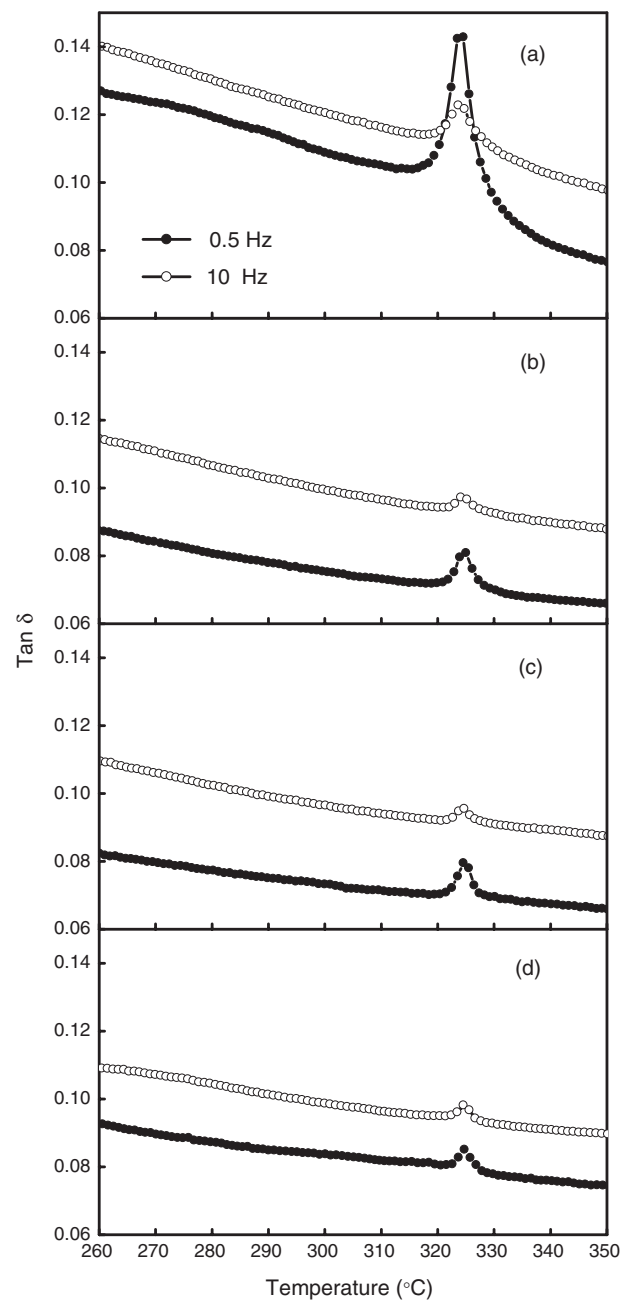


**Figure 4.** Internal friction  $\tan \delta$  versus temperature at different frequencies (0.5, 10 Hz) with a heating rate of  $2^\circ\text{C min}^{-1}$  for the pure Al sample.

The Clausius–Clapeyron equation shows that a change  $\Delta P$  of external stress provokes a change of the melting temperature by an amount  $\Delta P(v_l - v_s)/(s_l - s_s)$ , where  $v_l$  and  $v_s$  are the molar volumes of the liquid and the solid phases, respectively, and  $s_l$  and  $s_s$  are the corresponding molar entropies [25]. The latent heat of fusion for Pb is  $4.81 \text{ kJ mol}^{-1}$  [26], the density of solid Pb is  $11.3 \text{ g cm}^{-3}$  and the density of liquid Pb is  $10.7 \text{ g cm}^{-3}$  [27], from which the molar entropy change  $s_l - s_s = 8.01 \text{ J K}^{-1} \text{ mol}^{-1}$  and molar volume change  $v_l - v_s = 1.02 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$  are obtained. Substituting  $s_l - s_s$  and  $v_l - v_s$  into the Clausius–Clapeyron equation, we obtain the following expression:  $\Delta T = 1.27 \times 10^{-7} \Delta P$ ; here  $\Delta P$  is in  $\text{N m}^{-2}$  and  $\Delta T$  is in K. The stress distribution in the sample is not homogeneous. When the sample experiences a maximum stress of  $4 \times 10^7 \text{ N m}^{-2}$  the melting temperature change is about  $\Delta T = 5.08 \text{ K}$ . Thus an increase in the external stress will generally increase the melting temperature, i.e., the stress will influence the melting point. If the melting temperature increases, the molten fraction will decrease. In contrast, the molten fraction will increase with the decrease of the melting temperature. That is to say, the molten fraction of a particle will depend on the stress.

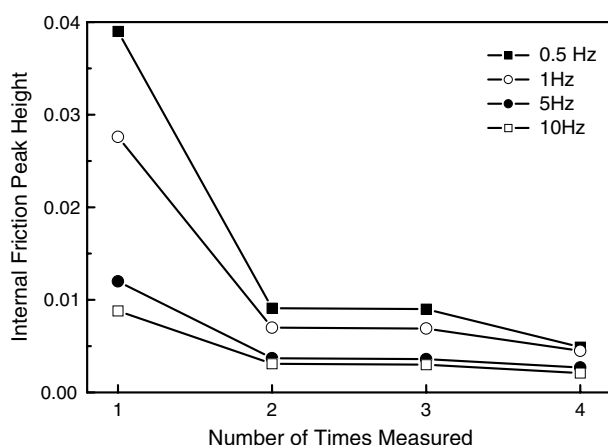
In DMA measurements, a periodic sinusoidal stress is applied to the sample, and the Pb particles will feel alternative tension and compression stress, which may change the melting temperature of Pb particles cyclically. So the surface molten fraction of a particle is changed cyclically. It is the alternative stress field that causes the melting/solidification process at the surface of a particle. The melting/solidification process creates the vibration energy dissipation and causes the internal friction peak. When the temperature increases, the molten fraction of a Pb particle increases; this is caused by external heat energy. However, the periodic melting/solidification process that happens on the surface molten layer will still remain on the surface of the particle until the whole particle melts.

The surface melting can happen over a very large surface area for n-Pb particles because of the enhanced surface-to-volume ratio. The Pb particle size in the as-prepared Al–5 at.% Pb sample is the smallest, so a very strong internal friction peak can be obtained and  $H_1$  is the largest for the first measurement. After the first heating measurement, the Pb particles have coarsened. So the size of Pb particles in the sample for the second DMA heating measurement is larger. In this case the particles' surface area decreases compared with the sample for the first measurement, which makes  $H_2$  decrease. Because the temperature condition of the second



**Figure 5.** Internal friction  $\tan \delta$  versus temperature at different frequencies (0.5, 10 Hz) with a heating rate of  $2^\circ\text{C min}^{-1}$  for the Al-5 at.% Pb at the (a) first, (b) second, (c) third and (d) fourth measurement. Before the fourth measurement the sample had been annealed at  $500^\circ\text{C}$  for 2 h.

DMA heating measurement is the same as that of the first measurement, the size distribution of Pb particles in the sample for the third heating measurement is approximately equal to that for the second heating measurement, which makes  $H_3$  approximately equal to  $H_2$ . After being



**Figure 6.** The height of the internal friction peak,  $H_n$ , at different frequencies versus the number of times it is measured.

annealed at 500 °C for 2 h, the Pb particles grow much larger, resulting in the surface area decreasing further; as a result,  $H_4$  is much smaller than  $H_3$ . The value of  $H_n$  corresponds to the size distribution of Pb particles with different surface-to-volume ratio.

#### 4. Conclusions

The internal friction technique has proved to be a suitable method for studying surface melting behaviour. There is an internal friction peak appearing around the Pb melting point and the internal friction peak height decreases with the increase of n-Pb particle size. A melting/solidification process occurring on the surface of n-Pb particles during internal friction measurements accounts for the internal friction peaks. The results may throw useful light on understanding the nature of material melting and explaining the common phenomenon of surface melting.

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