Melting and solidification of Pb nanoparticles embedded in an Al matrix as studied by temperature-modulated differential scanning calorimetry

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Abstract

A newly developed temperature-modulated differential scanning calorimetry has been used to study the melting and solidification processes of Pb nanoparticles embedded in an Al matrix under continuous heating and cooling conditions at rates of 1–5 K min⁻¹. Endothermic peaks have been observed in the total, the reversing and the non-reversing heat flows during the melting process, indicating that the process is controlled by both thermodynamics and kinetics. As the underlying heating rate increases, the enthalpy change in the reversing heat flow increases whereas that in the non-reversing heat flow decreases, while that in the total heat flow remains constant. On the other hand, during solidification, exothermic peaks are observed only in the non-reversing and total heat flow curves and the enthalpy changes remain essentially constant when the underlying cooling rates increase from 1 to 5 K min⁻¹. No exothermic peaks were observed in the reversing heat flow curve. This indicates that the solidification process is controlled essentially by kinetics.

§ 1. Introduction

Differential scanning calorimetry (DSC) is a widely used method to measure heats and temperatures for various phase transitions which involve thermal effects. In DSC measurements, the sample temperature is either ramped linearly at a constant heating (or cooling) rate or kept constant as in isothermal experiments. The measured heat flow can be described by the following equation:

\[ \frac{dH}{dt} = -c_p \beta + f(T, t), \]

where \( H \) is the amount of heat evolved, \( c_p \) the heat capacity, \( \beta \) the heating rate, \( T \) the absolute temperature and \( t \) the time. It states that the heat flow measured in a DSC cell, which is referred to as total heat flow (HF), is made up of two terms. The first term is a function of the heat capacity of the sample and the heating rate, which is
denoted as the thermodynamic or reversing heat flow (RHF). The second term is a function of absolute temperature and time, which governs the kinetics and is denoted as the non-reversing heat flow (NHF). The measured heat flow in DSC is the total heat flow including both the RHF and the NHF.

Recently, an enhanced version of the DSC method, temperature-modulated differential scanning calorimetry (MDSC) has been introduced (Reading 1993, Reading et al. 1993). The benefits of the MDSC method have been documented in several recent publications (O’Reilly and Cantor 1996, Ishikiriyama et al. 1997, Ishikiriyama and Wunderlich 1997). One of advantages of the MDSC is that it is able to separate the RHF and the NHF from the HF during a phase transition. In MDSC, the sample temperature is modulated sinusoidally about a constant ramp so that the temperature at time $t$ is

$$T = T_0 + \beta t + A \sin \left( \frac{2\pi t}{p} \right),$$

where $T_0$ is the initial temperature, $A$ the amplitude of the modulation and $p$ the period. The resulting instantaneous heating rate $dT/dt$ varies sinusoidally about the average underlying heating rate $\beta$. The apparatus measures the amplitude of the instantaneous heat flow and the average heat flow (which is the HF). By carrying out a suitable Fourier deconvolution of the measured quantities, both the RHF and the NHF can be determined. It is noted that no such information could be determined hitherto with the conventional DSC method.

The melting of crystalline solids is an important phase transition in materials science. The special capability of MDSC to separate the RHF and the NHF from the signals makes it useful to study the first-order phase transitions such as melting and solidification (O’Reilly et al. 1996). MDSC has been used to investigate melting and crystallization processes in several polymers and in pure In under quasi-isothermal condition (Ishikiriyama et al. 1997, Ishikiriyama and Wunderlich 1997). However, no experimental results have been reported to date on melting and solidification in metals using MDSC under the condition of continuous heating. This is probably because melting of metals normally takes place within a very narrow temperature range (a few kelvins) during heating, a range within which it is difficult to collect accurately four modulated cycles for a Fourier deconvolution. The collection of at least four modulated cycles within a transition is a basic requirement for MDSC to work properly. Recently it was reported that the melting of the Pb nanoparticles embedded in an Al matrix took place over a temperature range of about 30 K as determined by a conventional DSC (Sheng et al. 1996). This made it possible to study the melting behaviour of pure metals by MDSC, since for such a large temperature range the four modulation cycles are easily collected. In this work, we present the first MDSC study on the melting and freezing of metals under continuous heating and cooling conditions with the aim of revealing new information about these transformation processes.

§ 2. Experimental details

Commercial elemental powder blends of Al and Pb (purity, 99.999%; particle size, less than 100 mesh) with a composition of Al–10 wt% Pb were used as starting materials for ball milling. Ball milling was performed in a vibratory ball mill protected by an Ar atmosphere. High-hardness chrome steel balls of good wear resistance were used; the ball-to-powder weight ratio was 30 to 1 and the milling time was
10 h. The as-milled Pb-Al samples were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Both XRD and TEM experiments indicated that the as-milled product was a nanostructured mixture of pure Al and Pb phases and no alloying effect between Al and Pb was observed. The mean particle size of Pb estimated from XRD and TEM measurements was about 15 nm. The shape of the Pb nanoparticles embedded in the Al matrix was irregular and no epitaxial orientational relationship between Pb and Al could be identified from TEM observations. This means that random incoherent interfaces were formed between Pb and Al in the as-milled samples.

The MDSC experiments were carried out on a temperature-modulated differential scanning calorimeter (TA Instruments Inc. USA) using a refrigerated cooling system and a N$_2$-gas DSC cell purge. The modulated DSC regime was used to measure the modulated heat flow in both heating and cooling up to 400 °C. In order to obtain accurate and reproducible results, three experimental parameters need to be controlled in MDSC measurements, namely the underlying heating rate, the oscillation amplitude and the oscillation period. The underlying heating and cooling rates were from 1 to 5 K min$^{-1}$, with the oscillation amplitude between 0.1 and 0.2 K and the modulation period from 40 to 60 s. The oscillation amplitudes and periods were determined so that at least four modulation runs could be performed during melting and freezing of Pb nanoparticles and the modulated heating and cooling rates were above 0 K min$^{-1}$. Figure 1 illustrates the modulated heating flow and modulated heating rate for a MDSC run at a underlying heating rate of 2 K min$^{-1}$, showing good control of conditions. The MDSC runs were repeated for the same sample of about 40 mg at least three times, and measurements of temperature and enthalpy changes were made on the third run.

![Figure 1](image_url)
§ 3. Results and discussion

Figure 2(a) shows MDSC results obtained at an underlying heating rate of $2\text{K min}^{-1}$ with an oscillation amplitude of $0.2\text{K}$ and a period of $60\text{s}$. Evidently there is an endothermic peak in the HF corresponding to the melting process of Pb nanoparticles. The onset temperature is determined to be $317.4^\circ\text{C}$, which is about $10^\circ\text{C}$ below the equilibrium melting point for Pb bulk crystal ($327.2^\circ\text{C}$). The melting-point depression for the Pb nanoparticles embedded in an Al matrix was discussed by Sheng et al. (1996) and was attributed to the increase incoherent Pb–Al interfaces which acted as heterogeneous nucleation sites for the melting of Pb. A summary of characteristic temperatures obtained by MDSC under various underlying heating and cooling rates is given in Table 1. The integrated peak area, that is the total enthalpy change during melting of Pb nanoparticles, is about $10.1\text{J g}^{-1}$(Pb), which is also smaller than the fusion enthalpy change for bulk Pb ($24.0\text{J g}^{-1}$) (Smithells and Brandes 1976). Such a depression arises from the increase in Pb–Al interfaces, as addressed by Sheng et al. (1996). Endothermic peaks were detected corresponding to the melting process in the RHF and NHF curves respectively, which have similar shapes and characteristic (onset and peak) temperatures as those in the HF curve. The enthalpy changes for the RHF and NHF peaks are $5.7\text{J g}^{-1}$ and $4.0\text{J g}^{-1}$.

![Figure 2](attachment:image.png)

Figure 2. (a) HF, RHF and NHF functions of temperature under a underlying heating rate of $2\text{K min}^{-1}$ showing endothermic reaction during melting of a Pb nanoparticle embedded in an Al matrix.
respectively. The sum of these two enthalpy changes (9.7 J g\(^{-1}\)) is close to the HF (10.1 J g\(^{-1}\)). The enthalpy change in the RHF is a measure of energy absorbed by the sample to raise its heat capacity, that is the thermodynamic enthalpy change. The enthalpy change in the NHF, however, is the energy absorbed by the sample to drive the melting process kinetically. The above results clearly indicate that the melting process of Pb nanoparticles embedded in an Al matrix under an underlying heating rate of 2 K min\(^{-1}\) is controlled by both thermodynamic and kinetic processes.

Figure 2(b) shows the MDSC results obtained at an underlying cooling rate of 2 K min\(^{-1}\) with an oscillation amplitude of 0.2 K and a period of 60 s. An exothermal peak is seen in the HF curve, indicating a solidification process of the liquid Pb nanoparticles. A similar exothermal peak is detected in the NHF curve, but no exothermal peak is seen in the RHF curve, apart from a tiny bump. The integrated peak area for the HF peak is roughly equal to that for the NHF peak for the freezing of Pb. This result indicates that the freezing process of Pb nanoparticles embedded in an Al matrix under a cooling rate of 2 K min\(^{-1}\) is mainly kinetically controlled. Repeated heating and cooling MDSC measurements yield consistent results for melting and freezing in the Pb–Al nanogrannular sample.

Table 2 lists the enthalpy changes in the HF, the NHF and the RHF curves as functions of heating or cooling rate from 1 to 5 K min\(^{-1}\) respectively. It is seen that, with increasing heating rate, the RHF enthalpy change increases and the NHF enthalpy change decreases, while that of the HF remains constant (figure 3). An increase in the underlying heating rate results in a decrease in the energy fraction for the kinetic process of melting. At an underlying heating rate of 5 K min\(^{-1}\), the NHF
curve is essentially flat and no endothermic peak can be detected, while the RHF enthalpy change increases to a value equivalent to that in the HF. This implies that the energy absorbed by the sample at a underlying heating rate of 5 K min\(^{-1}\) is totally used to raise the heat capacity. No energy is used to drive the kinetic process of melting due to the fast heating rate. On the other hand, in the solidification process, there is no cooling rate dependence of enthalpy change in the NHF and the HF, both being 14.5 J g\(^{-1}\) at the cooling rates studied. This clearly confirms that the solidification process is essentially a kinetically controlled process.

Finally, figure 4 shows the volume fraction melted as a function of temperature for the HF, the NHF and the RHF curves for a sample heated at a underlying heating rate of 2 K min\(^{-1}\). In conventional DSC measurements, the melting kinetics of a solid are normally analysed by means of the HF signals, which basically consists of both the kinetic and the thermodynamic contributions. By separating the HF into the RHF and the NHF in the MDSC measurement, one can evaluate the melting kinetics more accurately in terms of the NHF signals, which specifically represent

Table 2. Heat changes during melting and solidification of Pb nanoparticles embedded in an Al matrix measured by MDSC.

<table>
<thead>
<tr>
<th>Underlying heating rate (K min(^{-1}))</th>
<th>Melting</th>
<th>Solidification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>RHF</td>
</tr>
<tr>
<td>1</td>
<td>11.2 ± 0.3</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>10.2 ± 0.2</td>
<td>5.7 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>9.9 ± 0.2</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>10.5 ± 0.2</td>
<td>7.3 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>10.0 ± 0.2</td>
<td>10.4 ± 0.2</td>
</tr>
</tbody>
</table>
information on transformation kinetics. By integrating the partial area of each endothermic peak in the three heat flow curves, one can obtain the volume fraction melted as a function of temperature (assuming that the enthalpy change is proportional to the volume of liquid from melting). It is seen that these three curves are very similar in shape. A very small temperature lag can be observed between the HF and the kinetic (NHF) signals, especially at the beginning of the melting. When the melted volume fraction exceeds 50%, the three curves merge together. The present result shows that the difference between the melting kinetics derived from the HF and those from the kinetic heat flow (NHF) is very small. This agrees with the previous observation in a melting study of Cd particles embedded in an Al matrix using conventional DSC as reported by Zhang et al. (1996). However, the measurements carried out in the present study are directly obtained from the thermodynamic and kinetic processes and are probably more accurate.

4. Conclusions

A newly developed MDSC has been used to study the melting and solidification processes of Pb nanoparticles embedded in an Al matrix under continuous heating and cooling conditions at rates of 1–5 K min\(^{-1}\). The results indicate that melting is controlled by both thermodynamic and kinetics, whereas solidification is controlled essentially by kinetics alone.
Figure 4. Volume fraction of melt as a function of temperature for the HF, the RHF and the NHF under an underlying heating rate of 2 K min\(^{-1}\).

REFERENCES