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Optimizing Contact Thermometry High-Temperature Fixed-Point Cells (>1,100 °C) Using Finite-Element Analysis

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Abstract The advent of high-temperature (i.e., metal–carbon eutectic) fixed points (HTFP) has placed high demands on the equipment needed to implement them. In particular, the HTFP performance is sensitive to the thermal environment. The temperature gradient in the crucible volume determines the duration and form of the melting plateau, and a gradient in the wrong direction along the crucible can result in mechanical damage. With an emphasis on crucibles for contact thermometry, a transient thermal model, which employs the finite element method is described. The aim is to optimize the HTFP environment, and to evaluate the relationship between the temperature of the liquid–solid interface (the actual fixed-point temperature) and the temperature measured by the contact thermometer (the measured fixed-point temperature). A simple mechanism to minimize temperature gradients along the HTFP cell axis is also presented. Importantly, the model shows that the actual temperature of the liquid–solid interface during melting is given by the indicated temperature at the end of the plateau, i.e., the liquidus point, not the point of inflection of the plateau, as is currently the convention. This does not significantly affect the conventional pure metal fixed points of the ITS-90, but could have ramifications for the new generation of high-temperature fixed points where the melt takes place over a temperature range and the liquidus temperature has yet to be identified.

Keywords Heat transfer · High temperatures · Melting · Modeling · Phase transitions

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1 Introduction

Temperature is one of the most commonly measured quantities in industry. As materials and alloys become ever more sophisticated, the demands on process control become more stringent and the uncertainties required for temperature measurement, and particularly control, become more exacting. National measurement institutes (NMIs) maintain reference standards, against which all other standards are calibrated. In thermometry, the reference temperatures are defined by phase changes of very high purity materials [1]. The melting and/or freezing of these fixed points are well-defined, reproducible phase transitions of matter, to which precise values of temperature can be assigned. For temperatures above 0.01 °C (triple point of water), fixed points are based on the melting or freezing temperatures of pure metals and, more recently, above 1,084.62 °C (freezing point of copper), metal–carbon (M–C) eutectic alloys [2]. While the fixed-point temperatures of specified metals (Ga, In, Sn, Zn, Al, Ag, Au, and Cu) are defined on the international temperature scale of 1990 (ITS-90) [3], above the freezing point of copper, there are no internationally agreed temperatures for eutectic fixed points. This latter issue is being addressed through the CCT-WG5 HTFP research program [4].

This work, focusing on HTFPs, seeks to identify, through thermal modeling, optimum operating conditions to obtain the best performance from these fixed points. There are many factors, which affect the quality of a melt, including the quality of thermal contact between the thermometer and the liquid/solid interface during the melt, the temperature uniformity throughout the fixed-point crucible, and the purity of the metal. In this article, the focus is on the propagation of the liquid–solid interface, its relation to the melting curve, effects of nonequilibrium melting, and the effect of the crucible environment. In addition, some methods for improving the quality of the melt are discussed.

2 Simulation of Melts

The implementation of fixed points based on metal–carbon eutectic alloys favors the melting point over the freezing point, since elemental diffusion leads to freezing-point temperatures, which are dependent on the rate of the preceding freeze. The present model does not include diffusion, and is, therefore, invalid for freezing points.

Figure 1 shows a typical crucible design for HTFPs for contact thermometry. This crucible is the basis for the finite-element model. For specified thermal conditions and melt initiation scenarios, the model calculates the temperature of a point at the bottom of the thermometer well as a function of time, the temperature distribution throughout the crucible, and the propagation of the liquid–solid interface. The physical situation is as follows. Starting from defined thermal conditions prior to melt initiation, the temperature of the furnace surrounding the crucible is ramped to a specified setpoint above the melting temperature, T_m. As the temperature of the outer wall of the crucible reaches T_m, the metal inside begins to melt, forming a liquid–solid interface, which gradually moves radially inward [5]. The temperature of the solid metal and crucible inward of the interface remains approximately constant at the melting temperature,

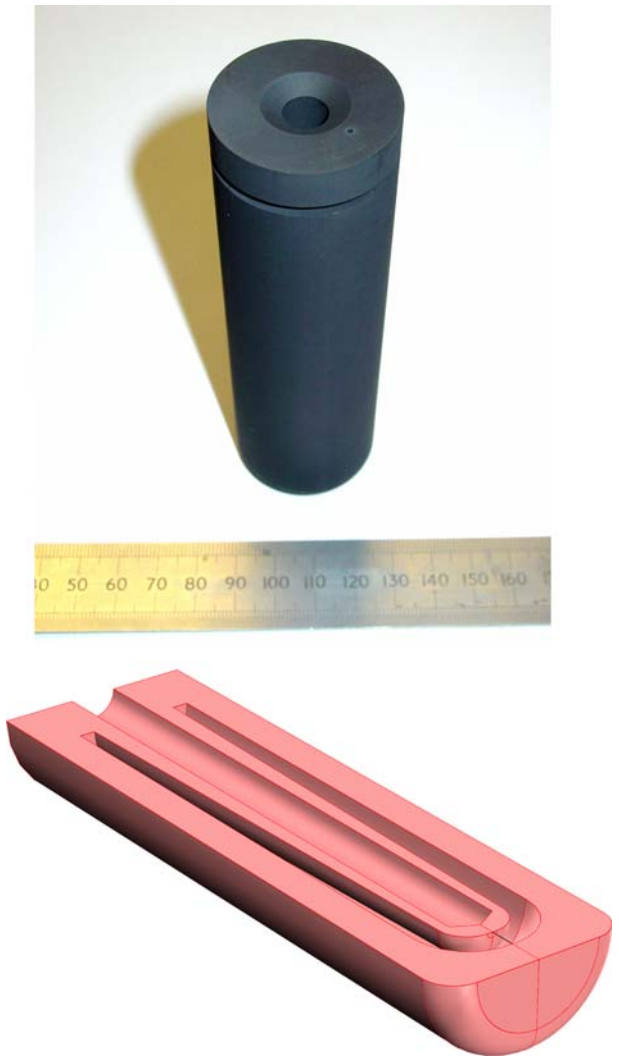

Fig. 1 Top: Fixed-point crucible. Bottom panel: cut-away drawing of the fixed-point crucible under consideration here, illustrating the central thermometer well, surrounded by the metal ingot

enabling the thermometer in the well to measure T_{m}. When the interface reaches the inner edge of the crucible, all the metal has melted and the crucible warms to the furnace set-point temperature.

The model is a two-dimensional (2D) axi-symmetric, transient heat transfer model. The key aspect is the modeling of the heat of fusion, which is performed by implementing a 'spike' in the temperature dependence of the heat capacity of the metal to yield an effective heat capacity C. The function chosen is of the form,

$$C\,(T) = C_{\mathrm{sl}} + (|T - T_{\mathrm{m}}| + \partial T_{\mathrm{m}})^{\gamma}\,, \tag{1}$$

where C_{sl} is the heat capacity of the solid and the liquid, here assumed to be invariant, T is the current temperature, T_m is the ITS-90 melting temperature, δT_m is a small constant, which represents a 'range', over which melting takes place to avoid a singularity at $T = T_m$, and γ is a critical exponent, which takes a negative value: in this case, $\gamma = -5$ as a starting value to provide qualitatively realistic results. This is an accepted method of dealing with phase changes in a computationally manageable way.

The model consists of two sub-domains: the pure fixed-point material and the surrounding graphite crucible. The initial boundary condition is that all sub-domains are at the starting temperature. The temperature of the outer wall of the crucible is then ramped up to the furnace set point, which is some temperature above T_m. The model is so constructed that the temperature of the crucible outer wall attains the set-point temperature quickly, before the melting plateau appears. All other boundaries are endowed with axial symmetry.

The temperature of the thermometer in the central well is approximated by the temperature of a point at the bottom of the thermometer well. Full simulation of a thermometer system (e.g., platinum resistance thermometer or thermocouple) inserted in the well would unnecessarily increase the complexity and reduce the clarity of the calculation.

The system described here is a cobalt–carbon eutectic fixed-point. This is currently the subject of vigorous research at various NMIs worldwide [6], including NPL [7]. The cobalt–carbon system is an ideal candidate for FEM simulation because the melting transition occurs over a broad range of temperature compared to pure metal fixed-point systems. This could be because of 'pre-melting' at grain boundaries [8,9], whereby the material at boundaries in the highly-granular solid melts at lower temperature than the bulk. The result is a broad $C(T)$ that changes slowly as a function of T, which means that calculation times are much shorter than for pure metal calculations where δT_m approaches zero. The Co–C eutectic melts at approximately $T_m = 1{,}597\,\mathrm{K}$, with an approximate width $\delta T_m = 0.1\,\mathrm{K}$. The specific heat capacity of Co–C is taken as that of the pure metal, $C = 442\,\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$, and assumed to be the same in liquid and solid phases. Its density ρ is $8{,}900\,\mathrm{kg \cdot m^{-3}}$, and its thermal conductivity k is $67\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. For the graphite crucible material, $C = 720\,\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$, $\rho = 2{,}100\,\mathrm{kg \cdot m^{-3}}$, and $k = 120\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. For these simulations, the initial temperature of the crucible is $T_{init} = 1{,}587\,\mathrm{K}$, and the final temperature is $T_{final} = 1{,}606\,\mathrm{K}$. These last two parameters were chosen to permit a comparison with good-quality experimental data. The detailed numerical expressions employed by the model are the default ones provided by the COMSOL heat transfer module [10]. The top panel of Fig. 2 shows the temperature of a point at the bottom of the thermometer well as a function of time, i.e., the melting curve. As the simulation starts, the outer wall of the crucible increases from T_{init} to T_{final}, and the fixed-point material warms up until it reaches T_m, at which point the heat from the furnace is absorbed by a liquid–solid interface, or melting front, which represents the phase change. As the melt progresses, and the melting front moves radially inward toward the thermometer well, the temperature at the thermometer well changes very little because the heat from the exterior wall is being absorbed by the melting front to drive the phase transition. This is reflected in the plateau of Fig. 2, and the degree,

to which the liquid–solid interface is in thermal contact with the thermometer well is shown explicitly in Fig. 3.

In the real world, the thermometer output during the melt plateau enables its calibration. With most conventional fixed points, the plateau is, flat to better than 0.1 mK, so there is no difficulty extracting the melting temperature to the required precision. However, the melting of high-temperature eutectic fixed points occurs over a wider range of temperatures, e.g., ∼100–200 mK for Co–C. A key question is, exactly which part of the melting curve should be taken as the melting point. The current convention is to take the point of inflection. One candidate for a more physically meaningful parameter is the liquidus point, which is the temperature, at which the entire bulk system becomes liquid. However, it is not obvious by eye, which part of the melting curve represents the liquidus point, nor is there an established procedure to determine that which suits all circumstances.

The lower panel of Fig. 2 shows the derivative of the calculated melting curve, dT/dt versus T, to illustrate the difference between the value of T obtained from the

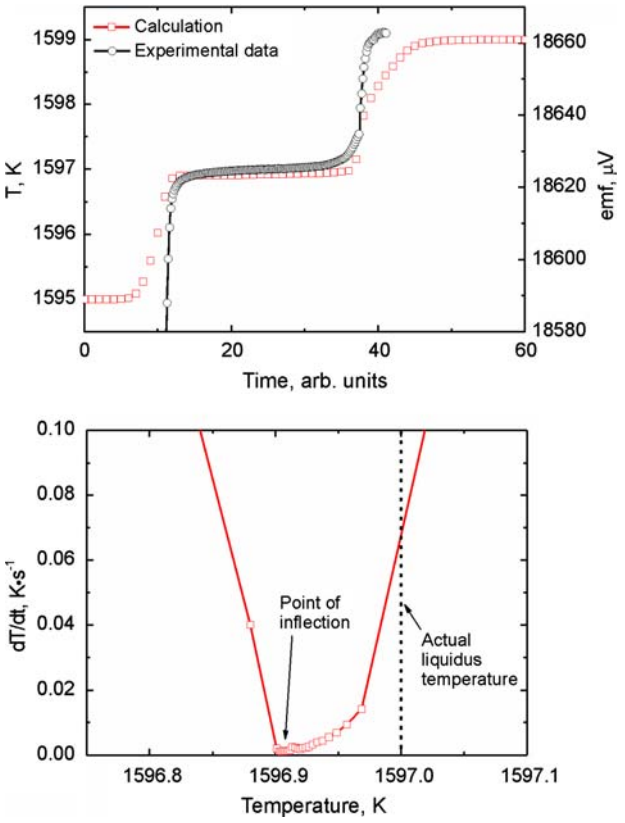

Fig. 2 Top: Calculated and measured melting curves for Co–C eutectic fixed-point. Bottom: dT/dt vs. T to show the point of inflection of the melt-plateau calculation, together with the actual melting temperature, which is an input parameter (location of spike in heat capacity $C(T)$). The calculation gives a point of inflection, which is 100 mK lower than the liquidus temperature

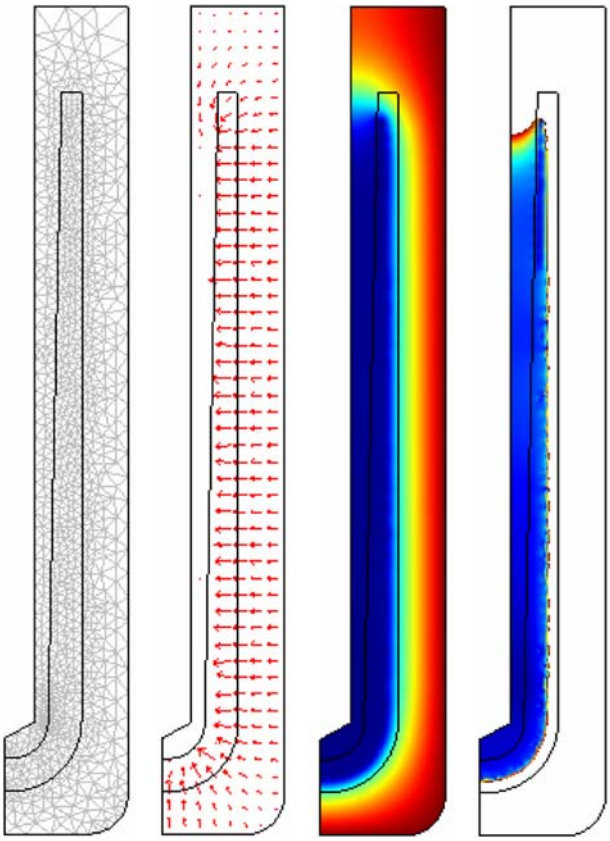

Fig. 3 Temperature distribution throughout crucible approximately half-way through a melt. First panel shows the mesh, second panel shows the heat flow, third and fourth panels show the temperature distribution, with a temperature range $T_m \pm 5\,K$ (third panel), $T_m \pm 0.5\,K$ (fourth panel). Note that the fourth panel illustrates the very close thermal contact between the liquid–solid interface and the thermometer—very important for determining the melting temperature

point of inflection (the current convention) and the value of the 'true' liquidus, i.e., the true melting temperature of the solid–liquid interface, when the last solid becomes liquid. The liquidus point can also be obtained from the experimental data, although the technique is currently in the early stages of development [9]. Nonetheless, the COMSOL results support the hypothesis that the melting temperature of the Co–C eutectic can be more reliably determined from the liquidus point than by the point of inflection, as is currently the convention.

3 Crucible Environment

It is clear that a good plateau is important in order to obtain a precise value of the melting temperature, but to obtain this, one requires a uniform liquid–solid interface, which propagates homogeneously and uniformly toward the center of the crucible. For

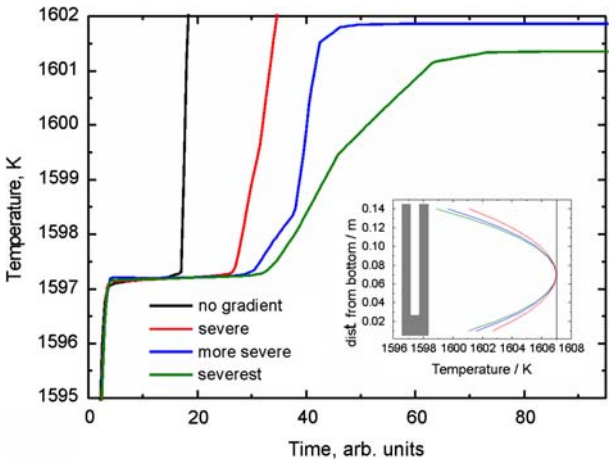

Fig. 4 Calculated effect of axial temperature gradients on the melting curve; the effect of higher temperature gradients is to introduce artifacts in the run-off region after the main part of the melt, where the inhomogeneity of the liquid–solid interface results in parts of the material remaining solid until considerably later on. This results in larger uncertainties in the calibration performed with such a curve. Inset shows the temperature gradients employed

this to happen, the temperature throughout the cell must be longitudinally uniform, i.e., there should be no temperature gradient along the axis of the cell. Figure 4 shows the effect of different temperature gradients imposed on the outside of the crucible wall on the achieved melt. Note the wide variation of the form and quality of the curve, especially at the 'run-off' after completion of the main part of the melt. These effects depend on the temperature gradient; these quantities translate directly to the uncertainty in the resulting thermometer calibration.

In practice, perfect uniformity is difficult to achieve because the axial temperature is typically only uniform over a short length, dropping rapidly on either side. At temperatures below approximately 1,000 °C, various devices such as sodium heat pipes and Inconel tubes can be used to smooth out or practically eliminate temperature gradients. Above this temperature, maintaining uniformity is more difficult, as the availability of materials to use as shields to smooth thermal gradients is severely limited, either because they melt or undergo adverse reactions with neighboring materials. In practice, one is constrained to use materials such as recrystallized alumina and graphite.

Besides plateau quality, for metal–carbon eutectic fixed points, there is another pressing reason for requiring temperature uniformity along the crucible, particularly for contact thermometry cells. Since the liquid is less dense than the solid, if the temperature is higher at the bottom of the cell during melting, the liquid, trapped by the solid above, has nowhere to expand, and therefore, breaks the fragile graphite crucible.

For these reasons COMSOL has been employed to evaluate two devices to minimize furnace temperature gradients. The first is a hollow graphite cylinder, with an inner diameter approximately 5 mm larger than the crucible diameter. Since the dominant heat transfer mechanism at high temperatures (e.g., above the copper point of 1,357 K)

is radiative [11], a gap between the crucible and the furnace will enable 'diffusion' of the temperature gradient because the entire crucible is within view of the entire range of temperatures along the external gradient [12]. The role of COMSOL was to verify that this proposal works (see upper panel of Fig. 5) and to optimize the dimensions of the tube. Here, the 3D static heat transfer mode is used, with conductive and radiative heat transfer mechanisms. An axial temperature gradient is applied to the outer edge of the outer cylinder. Interestingly, the calculation shows that the effectiveness of the device is not particularly sensitive to the crucible diameter; provided there is a gap, the temperature gradient is reduced to a tolerable level, i.e., by a factor of approximately three. When implementing such a device, the important consideration is to avoid physical contact of the outer sheath with the inner crucible. This information allows other design considerations, such as cost of crucible construction, and optimum geometry, to take priority.

The second device is a 'Swiss Roll' device (lower panel of Fig. 5), consisting of a flexible material coiled over several turns, with each turn radially insulated from the last [13]. This has the advantage that it does not rely on radiative heat transfer for its operation, so it will work at any temperature. This is created with the 3D static heat transfer mode, using conductive heat transfer only. A transient model was also examined. Again, an axial temperature gradient is applied to the exposed outer surfaces. Drawbacks of this device include reduced volume available for the crucible, and increased equilibration times. The calculation indicates that this device will eliminate the exterior temperature gradient, provided the roll material is sufficiently long. These are two examples of where simple COMSOL models have been employed to evaluate designs, which would be far too costly and time-consuming to develop and optimize experimentally on an individual basis.

4 Pre-melting at Grain Boundaries

To perform modeling of more realistic HTFP systems, one needs to take into account the pre-melting at grain boundaries, which have the effect of rounding the plateau. According to Gusarov [8], it is possible to represent the temperature dependence of the thickness of local equilibrium two-dimensional phases in polycrystalline systems as

$$h(T) = \left(\frac{a}{1 - T/T_{\mathrm{m}} + \delta(T)} \right)^{1/n}, \tag{2}$$

where a and n are weakly temperature-dependent parameters, $\delta(T)$ is a small positive value, a is taken as 0.35, and $n = 3$. The fraction of the total volume, which is liquid at a given temperature $T < T_{\mathrm{m}}$ is given as

$$v(T, t) \cong 1 - (1 - h(T, t)/d)^3, \tag{3}$$

where t is the elapsed time and d is the mean grain size. If the heat input and heat capacity are constant, then the volume $\mathrm{d}v$, which becomes liquid in a given time $\mathrm{d}t$, is

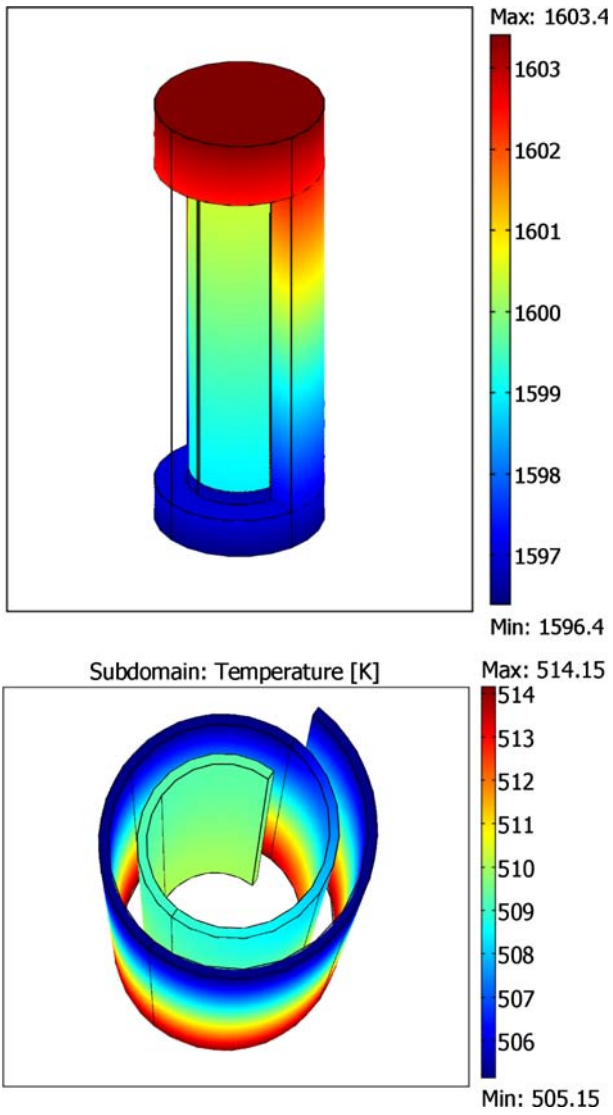

Fig. 5 Two devices for minimizing the temperature gradient along the crucible. Top panel shows a sliced view of a hollow cylinder with crucible inside, designed to diffuse the incident radiation. The crucible in the center is almost isothermal. Bottom panel shows a 'Swiss Roll' device (in this case for the Sn fixed-point), which is a piece of long, flexible material coiled around the crucible

proportional to dt. The dν can then be plotted as a function of T to yield the temperature dependence of a value proportional to the heat capacity, $C(T)$. This relationship is then employed in the finite element calculation. The effect of varying grain sizes calculated using this model is shown in Fig. 6. Here it is clear that although smaller grain sizes give rise to more pronounced curvature of the early part of the melting curve, the *liquidus* temperature determination is not significantly affected. Figure 7

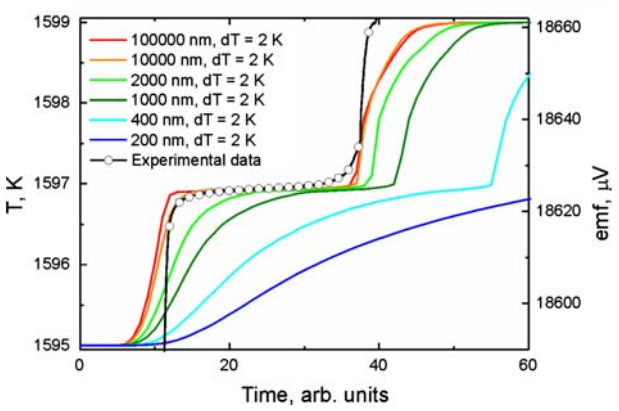

Fig. 6 Calculated effect of differing grain sizes on the melting curve, evaluated by adjusting a in Eq. 3, compared with an experimental melting curve measured with a type S thermocouple (points). Smaller grain sizes result in more melting at temperatures below T_m, which gives rise to more pronounced curvature at earlier times. However, this does not appear to significantly affect the liquidus point

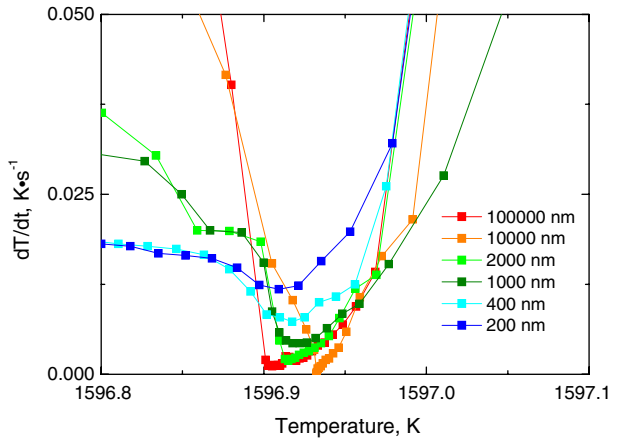

Fig. 7 Derivatives of representative curves in Fig. 6, illustrating the absence of systematic dependence of the inflection point on the grain size

shows the derivatives of the melting curves in Fig. 6, showing that the position of the point of inflection is, for the situation modeled here, only very weakly dependent upon grain size.

5 Conclusions

This article demonstrates the utility of COMSOL as a tool with which to evaluate the transient and steady state thermal behavior of fixed points in thermal metrology. The enhanced visualization of the propagation of the liquid–solid interface has given greater insight into how better to perform these melts and how to better design the

fixed-point crucibles to obtain the best possible quality melting curve. Key achievements of the model are:

- Optimization of the experimental setup to increase temperature uniformity;
- Insight into the temperature distribution throughout the crucible as the melt progresses;
- Evaluation of the difference between the point of inflection of the eutectic melting curve and the 'true' melting point;
- A simple evaluation of the effect of nonequilibrium melting, i.e., pre-melting at grain boundaries.

These are important areas of research because uncertainty in determining the melting point from the melting curve directly translates into uncertainty in the thermometer calibration. Future challenges are to extend these calculations to pure metal fixed points, where the melting occurs over a much narrower range of temperature, $\delta T_{\mathrm{m}} < 1\,\mathrm{mK}$, which is currently too narrow for computation with existing hardware.

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