Tzero™ DSC and Peak Shape of First Order Transitions

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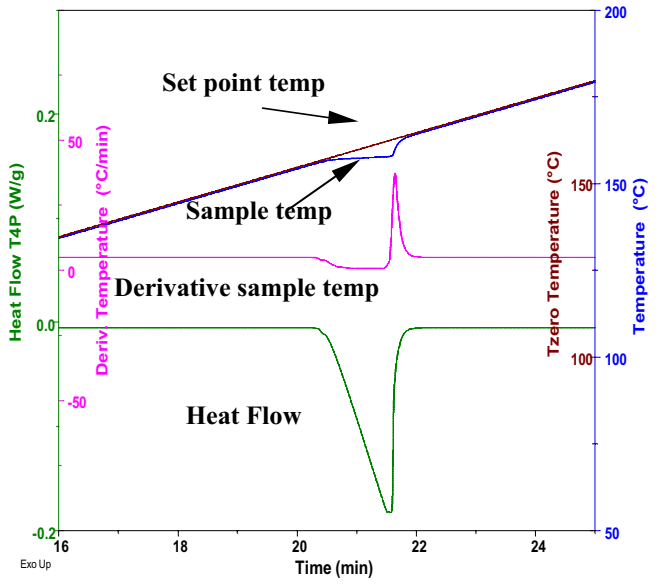
INTRODUCTION

Since pure indium metal is the primary calibrant for DSC, the shape of an indium peak is very familiar to thermal analysts. However, more is going on in a DSC when indium melts and crystallizes than is immediately obvious. In order to better understand Tzero™ technology and how it improves the analysis of first order transitions, here is a closer look at what happens in a DSC when indium melts and crystallizes.

Melting.

If heat is added at a steady rate to a crystalline material below the melting temperature, its temperature will increase until the melting point is reached. When a material melts there is a latent heat (or enthalpy) of melting. During melting, as more heat is added, the temperature of the sample stays constant as the latent heat is taken up. Once the sample is completely melted, the addition of more heat will again cause the temperature of the now liquid sample to rise.

Figure 1 - Melting a 350 mg indium sample



Melting in the DSC

When a DSC is heating, the cell is increasing in temperature at a constant rate. That is, the DSC furnace is controlled, using a sensor, a set point and a feedback circuit, to maintain a constant rate of temperature increase. In the TA Instruments DSC, a different sensor, the *sample temperature sensor*, monitors the temperature of the surface upon which the encapsulated sample is sitting. Figure 1 shows various DSC signals as indium is heated through its melting transition.

Before the indium begins to melt, the DSC set point is increasing linearly, and the sample sensor is also increasing linearly at a slightly lower temperature, due to thermal

and control lags between the sample and DSC cell temperature sensors. This is shown in the top two curves in figure 1.

As the indium begins to melt, energy flows into the sample side of the DSC cell to provide the latent heat of melting. This can be seen as the start of an endothermic peak, which is the bottom curve in figure 1. Since the temperature of the indium sample has now stopped increasing, and will remain isothermal until all the indium is melted, the sample sensor temperature also stops increasing, as can be seen in the second curve from the top. This effect can also be seen in the derivative of the sample temperature shown in the middle curve in figure 1, where the sample sensor temperature, that can be seen to drop to zero during the melt. Meanwhile, the DSC cell temperature continues to increase and the temperature difference between the sample and the DSC cell temperature increases linearly with time. This increasing difference leads to a linear leading edge of the indium peak since, according to Newton's Law of cooling (Ohm's law for heat), heat flow across a constant thermal resistance is proportional to the temperature difference.

After all the indium has melted, the melting endotherm reaches a maximum, and the differential temperature and heat flow to the sample begin to decrease. At this point the sample temperature has fallen behind the DSC cell temperature, as indicated by the sample sensor temperature in figure 1. This temperature now exponentially catches up with the set point temperature causing a brief spike in the heating rate, indicated by a peak in the derivative curve.

Thermal consequences of a non-linear sample temperature. This phenomenon is common to all DSCs, since it is caused by the thermal resistance between the sample and the DSC cell, and the time required for the latent heat to flow from the sensor to the sample. Moreover, because the DSC sample pan and the DSC sample platform are subjected to the non-linear temperature program (indicated by the derivative curve), the DSC curve contains two effects: the latent heat of melting of the sample, and the product of the pan heat capacity times the derivative sensor temperature. So, in order to obtain the heat flow to the sample alone, this asymmetric (one side of the DSC only) heating rate must be addressed. TA Instruments does this through Tzero™ and its Advanced Tzero™ technology (*1*, *2*). With this technology the heat flow is calculated using a four-term heat flow equation, with the fourth term being the asymmetric heating rate term, just mentioned.

Fusion/crystallization

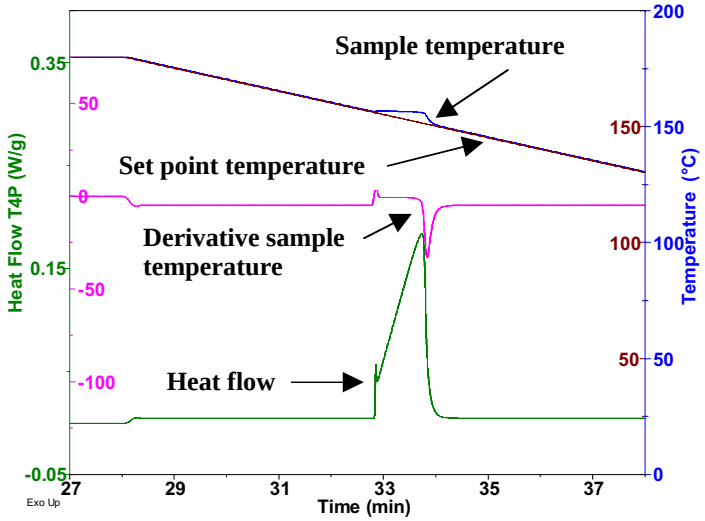
When a melted material is cooled below its thermodynamic melting point it will eventually crystallize. However, the nucleation or "seed" formation process makes this crystallization onset temperature uncertain. Once crystallization has started, the release of the heat of crystallization rapidly increases the temperature of the sample to the temperature of the thermodynamic *melt* temperature, as the Gibbs phase rule indicates there can be only one temperature in a single component, two-phase system. As more heat is removed from the sample, the sample will stay at its melt temperature until the entire latent heat of fusion has been removed (and the sample is completely solid.)

Crystallization in a DSC

As shown in figure 2, as a melted sample is cooled, the set point temperature decreases linearly and the sensor temperature follows somewhat behind in time.

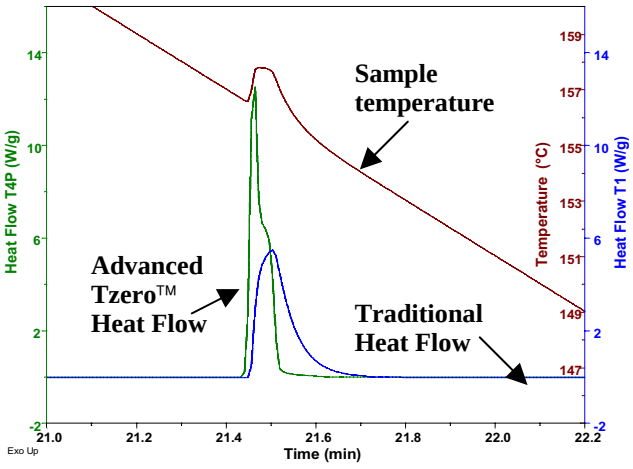
As it is cooled below the melt temperature, super-cooling and nucleation occur. At that point the temperature of the sample will rapidly increase up to the thermodynamic melting temperature and hold there until all the material has crystallized. This can be seen in the sensor temperature (top curve) in figure 2, and in the derivative of the temperature curve (middle curve) where the increase in sample temperature produces a small spike in the cooling rate. Once the sample has started to crystallize, the sample sensor temperature becomes nearly constant and the cooling rate (middle curve) goes back to zero, the level in the previous isotherm. While the sample temperature is constant, the cell temperature is continuing to decrease with the difference between the cell temperature and the sample temperature is widening linearly with time, producing a linearly increasing peak in the crystallization exotherm.

Figure 2 - Crystallizing a 350 mg indium sample



The peak shape produced by this event is an unusual one for thermal analysts, but its shape is completely consistent with expectation (*3*). It should be noted that the peak shape depends on the size of the indium sample, the pan mass (actually the pan Cp), the thermal resistance between the sample and the cell, and the degree of super-cooling. Hence, for a small specimen that has super-cooled a great deal (due to stabilization by surface tension), the fusion exotherm can be dominated by the initial spike as the sample attempts to return to the thermodynamic melting temperature before the entire sample has crystallized. (See figure 3.) This figure also shows the difference in peak shape between the Advanced Tzero treatment and the traditional treatment where only the first term in the four-term heat flow equation is utilized. The effect of Tzero and Advanced Tzero technologies is to avoid broadening the DSC curve; hence, it will dramatically

Figure 3 - Crystallization of a 4 mg indium sample, showing the effect on the sensor temperature and on the traditional DSC and Tzero heat flow data



sharpen the peak shape. When intermediate sized indium samples crystallize with super-cooling it is possible to observe a double peak. The peak shapes can look even more bizarre when viewed against a temperature scale axis. In this case, the sample temperature increase to the melt temperature in the middle of the fusion exotherm can result in a loop in the output.

After the crystallization is complete, the sample, pan and sensor temperature have fallen behind the program temperature and exponentially catches up, thus producing a spike in the cooling rate (middle curve, figure 2) and an exothermic tail on the traditional indium exotherm (but which is eliminated by Advanced Tzero™ technology).

Thermal consequences of a non-linear temperature program. As in the case of indium melting discussed above, whenever there is a change in the rate at which heat is flowing in or out of the sample (i.e., whenever, there is a sharp DSC peak) there is a resultant non-linear temperature program for the test sample and for the DSC pan. This produces a heat flow contribution, which, until now has not been separated from the heat flow produced by the sample specimen itself. It is this effect that is properly handled by using the four-term heat flow equation employed by Tzero technology.

CONCLUSION

While the Tzero technology may occasionally result in less familiar curve shapes, it is only because the traditional DSC curves masks what is really happening to the sample. The effect of peak broadening is well known for heating experiments, and obviously it also occurs under cooling conditions. Tzero technology uses an optimized DSC heat flux sensor design, combined with a four-term heat flow equation resulting in a more accurate sample heat flow and sharper peaks for first order transitions, both in heating and in cooling.

REFERENCES

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KEYWORDS

differential scanning calorimetry, metals, theory