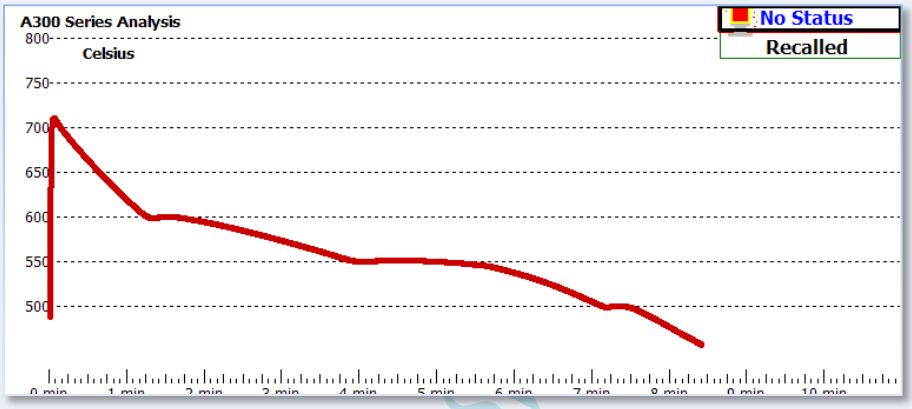
Thermal Analysis Metrics by derivatives

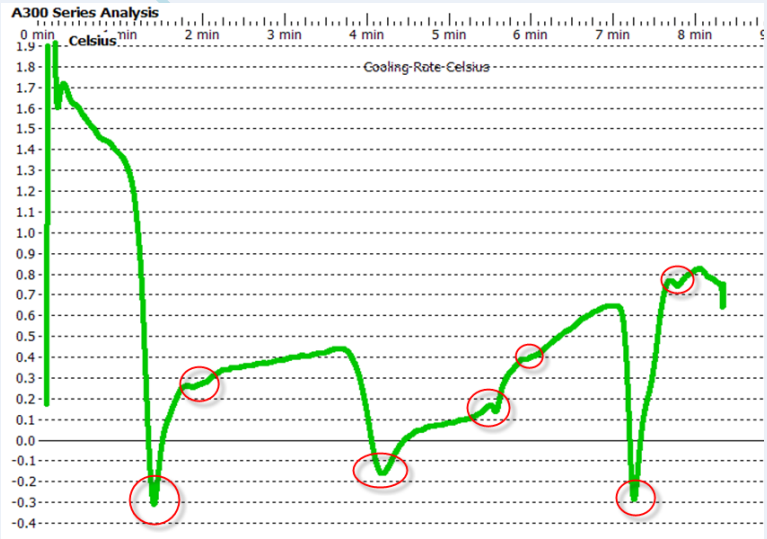
by David Sparkman Jan 9, 2010 all rights reserved

MeltLab took a bold step in introducing not just the first derivative but a whole series of derivative curves into the analysis system. A few research papers and an expensive instrument called a Digital Thermal Analysis (DTA) offer first derivatives, but no one else talks about the use of higher level derivatives. MeltLab has broken ground with noise filtering and smoothing techniques that are unique and allow as many derivatives as desired. Why use derivatives, and what do they give us? Let's talk.



Temperature curve A319 Aluminum

The temperature cooling curve has lots of information hidden in it in little bumps and squiggles that are almost invisible. But if the dT/dt (delta Temperature/delta time) curve is plotted, that information becomes visible. Some researchers show it as dT/dt, we have chosen what we think is a more intuitive way and flipped the plot over showing it as the cooling rate (-dT/dt). On this curve, exothermic events move the curve down, and endothermic events move the curve up.



Cooling curve A319 Aluminum showing thermal events

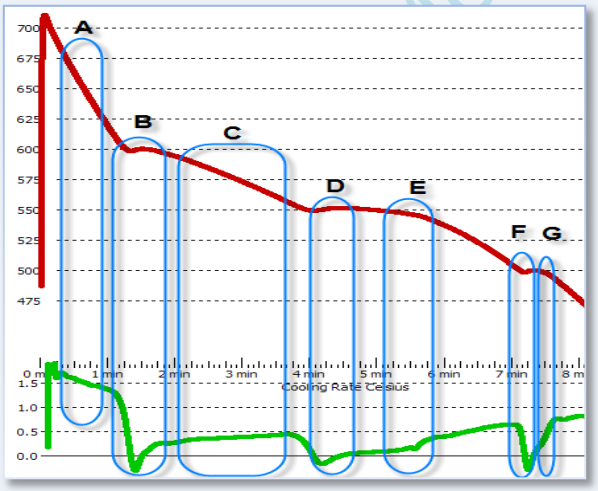
Exothermic events are caused when the atoms become more ordered (increased entropy), and endothermic events are caused when the atoms become less ordered (decreased entropy). On cooling, exothermic events give off heat, and endothermic events adsorb heat. Think of it as when you melt a metal, you have to put energy (heat) into the metal to pull the atoms further apart to make it a liquid, and you get that energy back when you let the atoms come back together into a solid. Remember that metal shrinks as it cools, so it expands as it is heated. If you look at the microstructure of a sample of metal, you will see different crystal structures. Many of these crystal structures have a different freezing point and produce some of the exothermic events seen in the cooling rate curve. Dr Backarud in his book Solidification Characteristics of Aluminum Alloys, Vol 2, Foundry alloys lists the following reactions for the A319.1 Alloy

1. 609 C Development of dendriteic network
2. 590 Formation of Al + $Al_{15}Mn_3Si_2$
3. 590 Formation of Al + Si + Al_5FeSi + $Al_{15}Mn_3Si_2$
4. 575 Formation of Al + Si + Al_5FeSi
5. 525 Formation of Al + Si + Al_2Cu + Al_5FeSi
6. 507 Formation of Al + Al_2Cu + Si + $Al_5Mg_8Cu_2Si_6$

For reference

$Al_{15}Mn_3Si_2$ is commonly referred to as Chinese script
Al_5FeSi is commonly referred to as beta crystals
Al_2Cu is a copper bearing grain boundary precipitant
$Al_5Mg_8Cu_2Si_6$ is commonly called magnesium silicide

Further reading reveals that these temperatures are influenced by cooling rates. Sigworth mentions that slow cooling rates can allow item 2 to even precede item 1. In the following thermal analysis, I have circled some of the areas where arrests are taking place, or might take place.



Selected areas of arrests in A319

A is preliquidus where some chinese script may appear.
B is the liquids arrest or number 1 in the list above
C is the dendritic growth area where arrests 2 and 3 may take place (Chinese Scrip or Beta Crystals)
D is the eutectic arrest
E is an undocumented arrest and some endothermic reaction.
F is number 5 where the copper percipitates in the grain boundries.
G is a slight additional exothermic reaction where number 6 or the Magnesium Silicide is coming out.

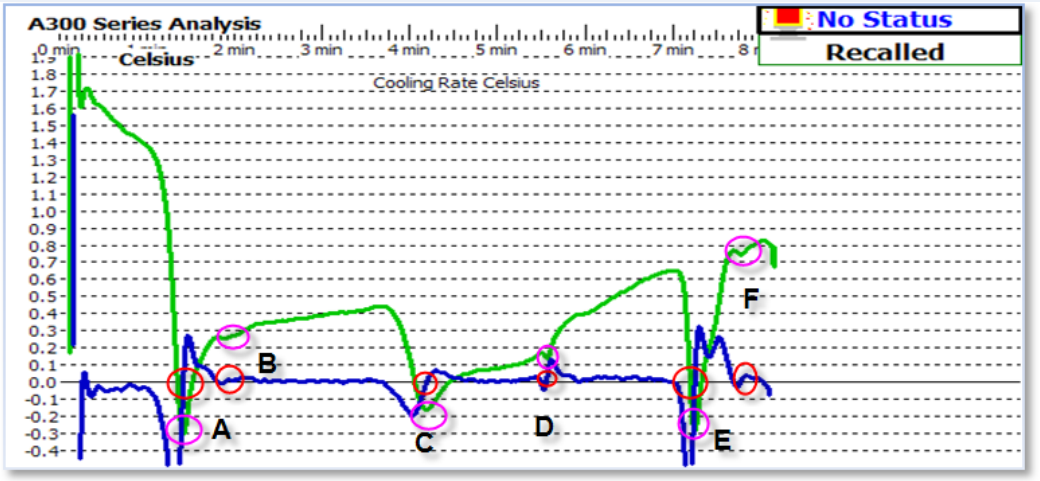
As can be seen by this graphic, not everything is in the book yet. An unexplained downward bump (exothermic) is happening at about 540 degrees (Area E), and is followed by an upward bump (endothermic).

This endothermic reaction at 540 is a disorder reaction. It is the formation of an interior surface within the molten metal: a gas bubble, a shrink or a void. It is believed that gas bubbles appear early in the eutectic and are less endothermic than shrinkage defects (the escaping gas provides some of the energy to form the interior surface), so I would call this one a shrink.

And if you are a picky investigator, you might notice another unidentified exothermic reaction right after the G area. So the cooling rate or inverted 1st derivative shows a lot that is already understood, and some things that are not yet described in the literature.

Metrics by Derivatives

The next step is to apply metrics to the curve. The first metric to find is a temperature for the strongest point of the arrest. Fortunately derivatives provide the answer.



2nd derivative (blue) added to cooling rate (Green) curve. Pink circles are arrests, red circles show 2rd derivative positive crossing points

The 2nd derivative always passes through zero in a positive direction (going up) at the strongest part of an exothermic (going down) arrest. Since it is very easy to tell the computer to notice the derivative going positive, we have the point on the x-axis from which we can know the temperature of the sample.

Pseudo Computer Code

```
For count:= 2 to maxReadings do
  If (derv2[count-1] < 0) and (derv2[count} >= 0) then
    ArrestTemp:= Temperature[count];
```

It is a little more complex than that, but the pseudo code gives an idea of the method. The main problem with the code is that we want the blue line crossing the zero axis sharply, and to ignore the crossovers when the blue curve is just clinging to the zero axis. So we introduce the 3rd derivative.

3rd derivative (rust colored) added to 2nd derivative and cooling rate

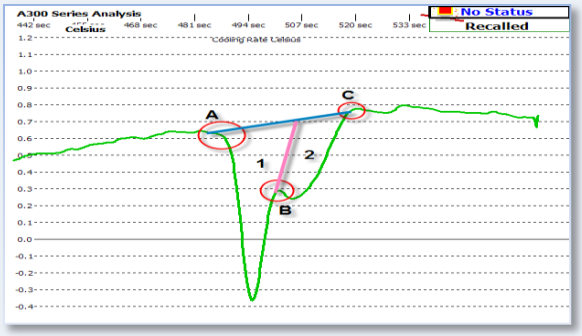
The 3rd derivative is actually the slope of the 2nd derivative, or how steeply the 2nd derivative is climbing or falling. So if we are looking for strong crossovers, we just add a condition that the 3rd derivative must be positive and greater than or equal to the 0.1 line on the graph. The scaling for the 3rd derivative on the graph in this figure is set to 50 times the cooling rate scale. So we are looking for 3rd derivatives greater than or equal to 0.002.

Pseudo Computer Code

```
For count:= 2 to maxReadings do
  If (derv2[count-1] < 0) and (derv2[count} >= 0) then
    If (derv3[count] >= 0.002 then
      ArrestTemp:= Temperature[count];
```

Thus we have a temperature at which the strongest point of each exothermic arrest occurred.

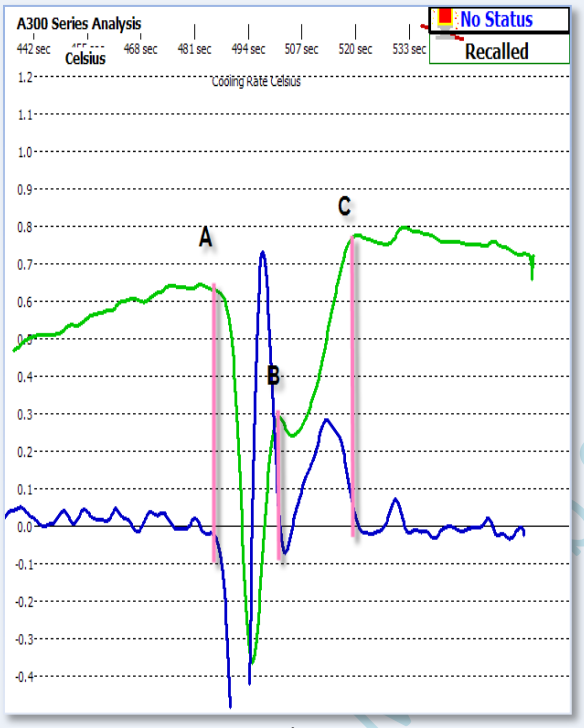
Additional Metrics – Getting at volume solid



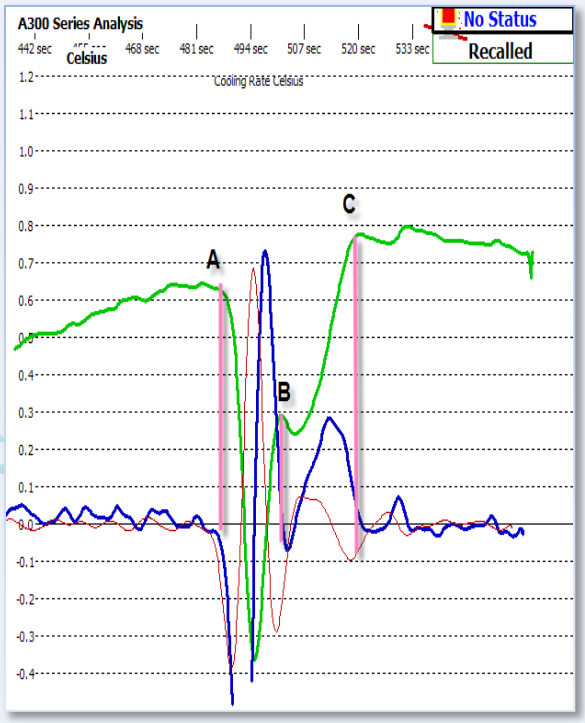
Grain boundary cooling rate of A319.2 alloy area 1 is due to Al_2Cu, area 2 is due to $Al_5Mg_8Cu_2Si_6$

There are several other items we would like to measure such as the coherency point, or the secondary dendritic growth, or the shrinkage arrest, but let's start with a different goal in mind. Can we measure the amount of energy produced by an arrest, ratio it against the total energy and come up with a measure of the volume solid of any particular crystalline structure? To do that we first need to determine the start and stop of each eutectic arrest.

For this exercise, I have chosen a different thermal analysis that is more interesting. This is the grain boundary cooling rate of a 319.2 alloy that contains a significant amount of magnesium and so has both a significant copper arrest (Al_2Cu) and a significant magnesium arrest ($Al_5Mg_8Cu_2Si_6$). The three red circles indicate in general the start of the copper arrest, the start of the magnesium arrest, and the general end of the two arrests. Draw a line between points **A** and **C** and the area below is the total energy of the two arrests. Extend a line from point **B** to the blue line and you divide the energy below the blue line into zone 1 (copper arrest) and zone 2 (mag silicide arrest).
So, how do we get the computer to do our work for us? We need to be able to find points **A**, **B** and **C**.

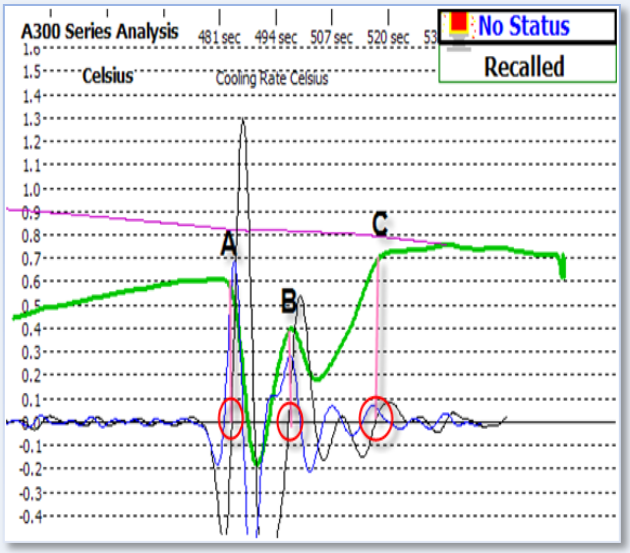


Cooling Rate and 2nd derivative



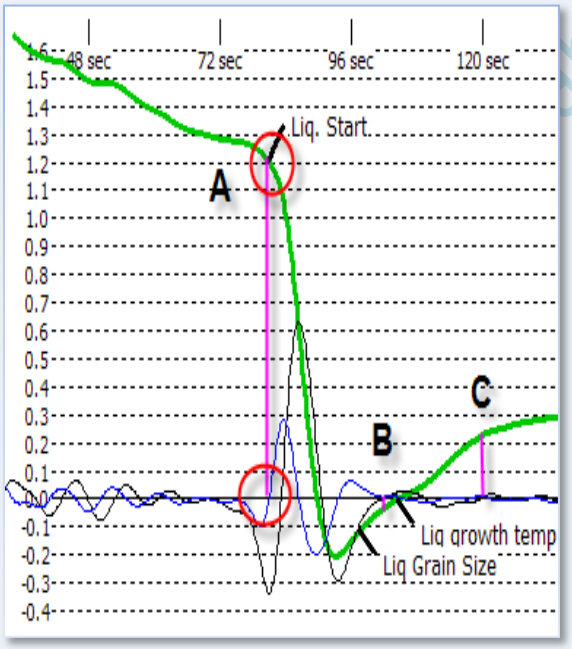
Cooling Rate, 2nd and 3rd derivative

It doesn't look good. We have a close match on B and the 2nd derivative, but not really on anything else. The 3rd derivative is no help either. What we really need in each case is to find where the green curve first starts to break away from its normal direction. We need the beginning of the beginning of the beginning of the arrest. Or in terms of the mathematicians: the beginning of the acceleration of the acceleration of the acceleration. Let's see what the 4th derivative looks like.



Cooling rate with the 4th derivative (black) and 5th derivative (blue) added. Pink lines are vertical drops from the three points A, B and C. Blue is the slope of Black. Red circles are 4th derivative positive crossovers.

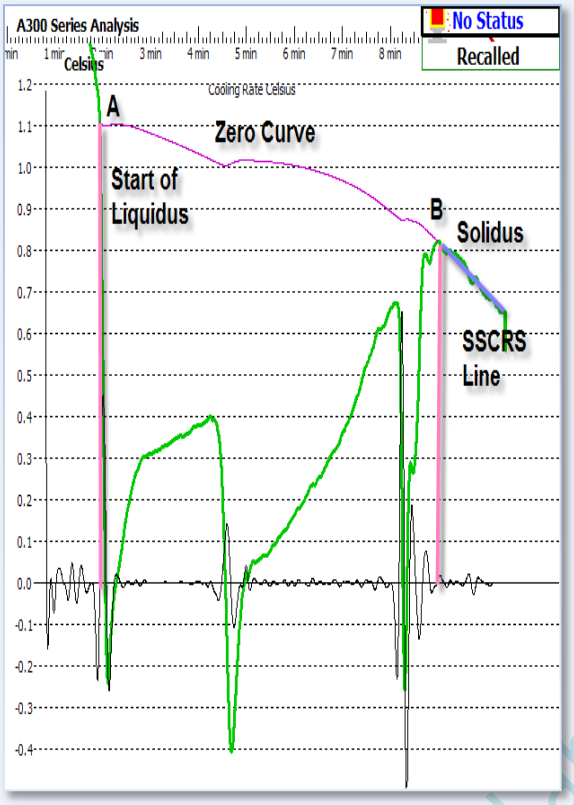
Not perfect but awfully close. In each case the 4th derivative is passing up through the zero axis at almost the same time that the green curve starts to bend away from its normal path – the beginning of the beginning of the beginning. The slight error is due to the smoothing algorithm that slightly shifts each derivative to the right. The answers are, as we engineers say, "Close enough". Again we will need to measure the slope of the 4th derivative as it passes through zero to filter out the zero crossovers due to background noise versus real events. But that is only the 5th derivative, and what is one more derivative among friends?



Start of liquidus by 5th derivative (blue)

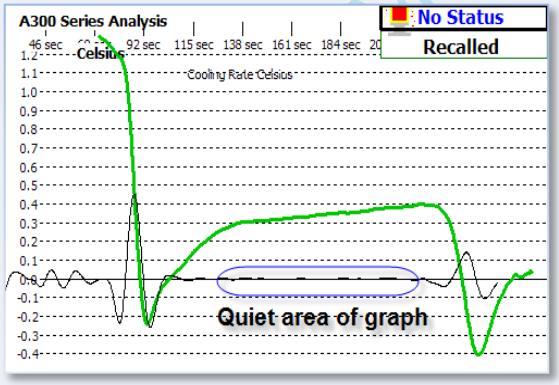
Here is the liquidus arrest. The 5th derivative predicts the start of liquidus (**A**) very well. Point **B** is determined by the 4th derivative. If you will notice, the slope of the green curve changes at **B**, so the interpretation is that point **B** is the end of the primary dendritic growth, and point **B** to point **C** with a different slope is the secondary branching growth, and the area beyond **C** is growth through dendritic thickening. It is a little trickier to teach the computer all of that, but it can be done. The "Start of Liquidus" is a very important point because it will be used to measure the total energy of solidification, and then each individual exothermic arrest will be ratioed against the total energy for a percent energy metric for each crystalline structure.

The Zero Curve Metric and the Noise Metric



Zero curve (pink) extending from start of liquidus to solidus point. Green curve is the cooling rate.

The zero curve was described for a long time as where the cooling rate would be if there were no actual exothermic events. Dr. Kierkus and Dr. Sokolowski of the University of Windsor were the first to successfully describe it mathematically. If we sum the total area between the zero curve and the cooling rate, we will have a measure of the total energy released during solidification. This energy can then be divided into the energy produced in any segment to give the percent of energy contributed by that crystallization event. Allowing that the specific heat of the various materials is not well known, we can say that the percent energy is "approximately" the same as the volume solid of that material. Should we get a better idea of the exact specific heat of some of these crystalline structures, we can then add a factor to get an improved volume solid. But for now, knowing that you have a 0.27% Magnesium Silicide will have to do.

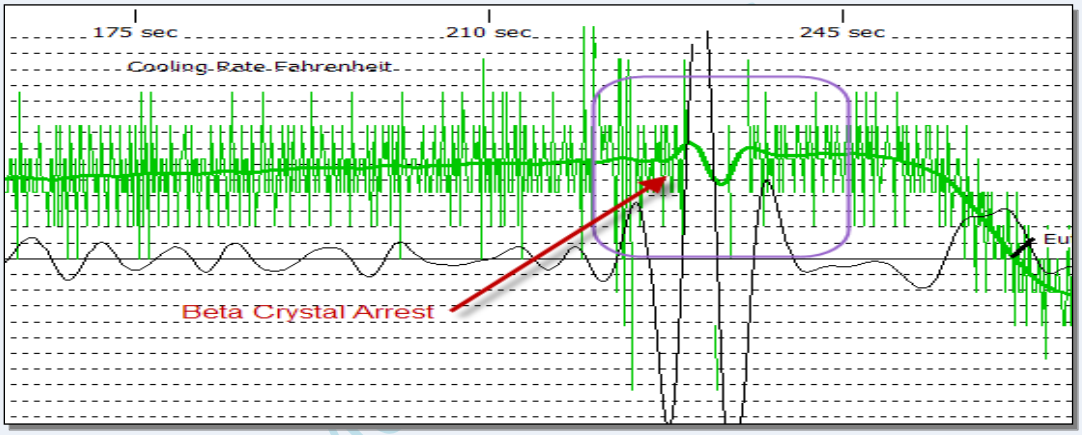


One final thought. If you examine the 4th derivative during certain sections of the thermal analysis, it is just a small vibration around zero. The TA exists in the computer as an array of data points for each curve and derivative. If we take a quiet area of the curve and perform a standard deviation on those values we come up with a value for the background noise of the curve: i.e. the normal variation when little is happening. This would be the standard deviation of the background noise (instrument noise, line voltage, RF energy, instrument precision, etc.). If this value is then compared against the strength of a 4th derivative "bump" of an unknown arrest, we can then calculate the variation of this arrest as how many standard deviations from background noise it is. If for example, the unknown arrest produces a 4th derivative value 3 times greater than the background noise, then we could

say that the probability of the arrest being real is statistically 99.7%. This metric may prove useful for evaluating very small arrests.

An embarrassing difference

At this point in time, we are unaware of any other commercial TA system that makes use of higher order differential curves. Part of it is the difficulty of filtering the data, both electronically and mathematically. We are much obliged to Jeff Burke, an electronics engineer by degree, who first worked out the hardware system. It has proven to be robust and long lasting. But the mathematics that allowed smoothing and filtering took many a long day and night working out, and the fine tuning continues. While it would be good to share this technology with the world, it puts the MeltLab system well ahead of the competition and puts food on our table. So for now it will remain a trade secret, though I am sure others can work it out… maybe.



Example of unfiltered/unsmoothed data and the final smoothed curve (green) as well as the 4th derivative (black). Note a slight endothermic reaction just before the start of the beta crystal growth.

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