Quantifying an Arrest in Thermal Analysis
by David Sparkman August 16th 2010 all rights reserved

Quantifying an arrest means to take the measure of the arrest – putting a number or, in this case, several numbers on an arrest. In figure 1 below, we have a pure arrest uncomplicated by additional arrests superimposed on the original. The green curve in figure 2 is the rate of cooling of a base iron curve. The Magenta line is the base curve or zero-curve, and the area between the two lines is the heat energy of solidification being given off by the metal as it cools. Obviously much more information can be seen in the rate of cooling than can be noticed in just the temperature curve.
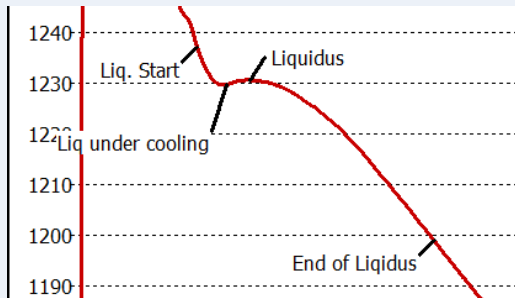

Figure 1 Temperature curve showing full liquidus area in a base iron. Recalesence is not common in the iron liquidus but does happen.
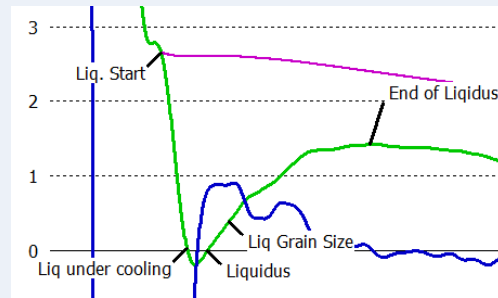

Figure 2 Rate of Cooling Curve of an iron sample with 2nd derivative is in blue. The zero-curve is in magenta. This is the same arrest as shown in figure 1.

Visually we can see that the rate of cooling starts bending down into the liquidus at the liquidus start point. It reaches its strongest point at the liquidus or in this case the liquidus growth[1] temperature as there was undercooling. And finally, it reaches the last of the liquidus phase and starts into the next (eutectic) phase at the end of liquidus point. In addition, the total energy of the arrest can be considered to be the area between the green curve and the magenta curve between the start and end of the arrest. A human being could locate these points easily enough, and a trained and skilled person could get very repeatable results. Teaching the computer to do this is another thing.
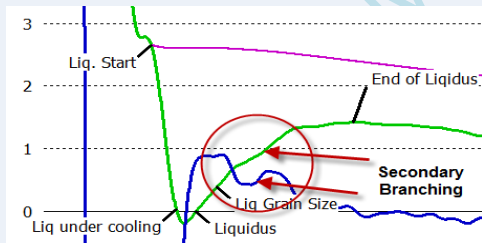

Figure 2 Rate of Cooling Curve of an iron sample with 2nd derivative is in blue. The red circle shows the characteristics of secondary branching.

Some additional points of interest are present in this example: the liquidus arrest produces enough heat to actually climb back up a little. This phenomenon is called recalesence or reheating and is caused because the metal under-cooled. We might want to measure this undercooling/recalesence. Some older equipment will mark the under cooling point as the liquidus. The correct point is the one shown above. It is referred to as the "Growth Temperature" by Bäckerud. This undercooling is caused by the combination of the speed of cooling, and the degree of inoculation. Faster heat removal promotes undercooling, and higher inoculation reduces undercooling.

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[1] The Growth temperature is a term coined by Dr Bäckerud. The temperature curve heats back up to a point that may be the arrest, or if the heat extraction is too rapid, may be slightly below the true arrest. If it is the true arrest, the curve will flatten out at the top. If there is no flattening, the true arrest is above the growth temperature. This applies to the liquidus as well as the eutectic, though the eutectic will generally show flatness as it is a longer arrest. The example above did not show flatness and so may be a degree or two below the true arrest for that chemistry. See Appendix for more detail.

The other point of interest would be information on dendritic arm spacing since this arrest in iron is due to dendrite formation. The dendrites produce energy faster if they have more surface area, hence they are more closely spaced. The maximum steepness of the curve at the Liq. Grain Size is determined by this dendrite spacing. The part of the green curve in figure 2 that is circled shows a slight downward inflection, an increase in energy production, while the blue line dipping indicates secondary branching of the dendrites.

So, although there is a great deal of information available in a single arrest, it takes a very well-trained person looking carefully at the curve to see it. What is needed is a way to extract the information in a reliable way automatically. So we introduce Calculus, a form of mathematics invented by Newton and Leibniz, to the system. Calculus is the mathematics of change, the study of acceleration and deceleration (derivatives), as well as the summing of complex accelerations (integration) which can be used to calculate the heat energies and then derive the percent of different microstructures.

Calculus has a function called derivatives or the rate of change. In our case, the rate of cooling is the rate of change of the temperature. For the purist, it is the first derivative inverted. Many university publications use the standard uninverted derivative, but I made a decision early on to use the more common term "rate of cooling" which a non-college educated user could understand. By definition, the second derivative then is the rate of change of the first derivative and can be used to find the minimum and maximum points of the first derivative. Those points are where the second derivative crosses zero: a test that a computer can do very easily.
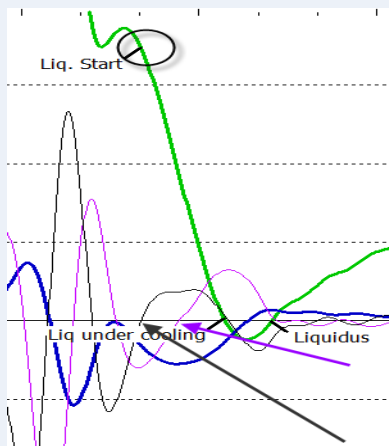

Figure 4. Magenta arrow points to zero crossing of the 3rd derivative or the steepest slope going into the arrest, and the black arrow points to the zero crossing of the 4th derivative or the beginning or start of the arrest.

To find the start of an arrest, what is needed is to find the very first indication of the curve bending from a normal cooling line toward the arrest. Figure 4 is a graph showing the second derivative (blue), the third derivative (magenta), and the fourth derivative (black) as they pass upward though zero (positive zero crossing). These zero crossovers also mark the lowest point of the previous derivative.

The last positive zero crossing of the 4th derivative before the arrest is used here to mark the start of the arrest. We also apply a rule that requires that the start point be in a range to prevent accepting a false signal. Depending on the alloy and sample size, this range is typically 1 to 4 degrees C. In my experience, this point should be at a higher rate of cooling than the end of liquidus, and the SSCRS (see appendix) point to qualify. Oxides and slag, as well as not enough superheat or too small of a sample, can interfere with finding this point.

The magenta point has sometimes been used as a grain size indicator (finer grains imply more crystals, faster growth). But, because this value is affected by the heat of the metal away from the thermal couple[2], the better indicator will be the slope coming out of the arrest.

Likewise, coming out of the arrest can be looked at in terms of the derivatives. The second derivative (blue) passes through zero when the rate of cooling maxes out. This marks the crossover point from the first major arrest (liquidus) to the next major arrest (eutectic). The first orange crossover (3rd derivative – far left orange circle) again

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[2] Heat travels ahead of the actual arrests, which move from the outside of the sample toward the thermal couple. This influences the curve going into an arrest, but has less influence coming out of an arrest, since the metal away from the thermal couple has already completed that arrest.

marks the steepest slope of the rate of cooling or the highest rate of heat production which relates to the dendrite arm spacing and in non-dendritic metals, the grain/cell size.
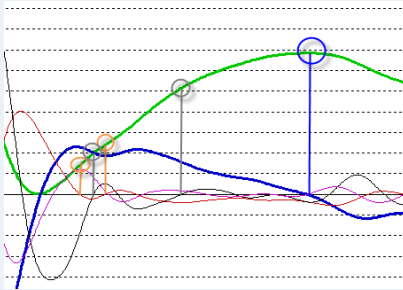

Figure 5. The 4th derivative (black) zero crossovers define the start of secondary branching as well as end of that branching. The 2nd derivative (blue) defines end of liquidus and start of eutectic arrest. The 3rd derivatives (orange) mark the steepest slope of the primary and the secondary dendrite arrests: they are used to calculate grain size or dendritic arm spacing.

The third derivative then quickly recrosses zero (positive pass) indicating the strongest point of secondary dendritic growth sometimes called dendritic branching. The gray curve (4th derivative) has two positive zero crossings in this area in this area. The first is the start of secondary branching and the second is the end of the secondary branching. A straight line between the two gray circles would enclose a small area which would be the amount of heat energy that could be attributed to this branching.

From these observations, we can take several arrest definitions for future use:

Measuring Major Arrests
1. Start of major Arrest – this is the positive zero crossing of the 4th derivative for independent arrests or, for major arrests that start during another arrest, it is the negative zero crossing of the 2nd derivative.
2. Arrest point of major arrest – this is the point of the strongest heat generation during the arrest. It is found on the positive zero crossing of the rate of cooling if there is recalesence or the positive zero crossing of the 2nd derivative if there is no recalesence.
3. End of major arrest – this is the first negative zero crossing of the 2nd derivative because there is always another thermal event even if it is only the solidus point: the point where the grain boundary freezes.
4. Grain size indicator – this is the first negative zero crossing of the third derivative after the arrest. It is controlled by the grain size for alloys like hypereutectic aluminum, or by the dendritic arm spacing for metals like hypoeutectic iron or aluminum.
5. Arrest energy – this is the integration or the summing of the area bounded by the start and end of the arrest, and the rate of cooling curve and the base or zero-curve. Because this is influenced by the size of the sample, this number is divided by the total energy between the zero-curve and the rate of cooling curve to give a percent of the total energy for this arrest.
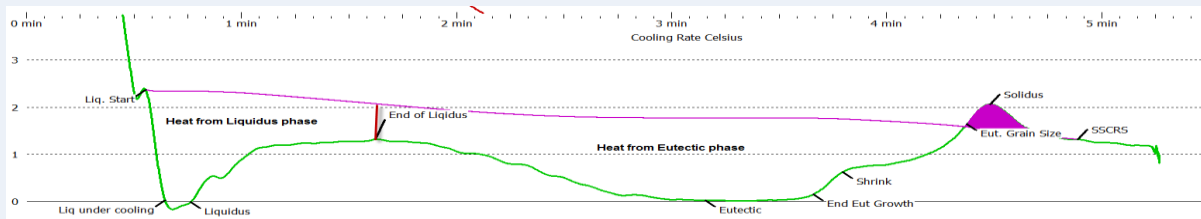

Figure 6. For a simple thermal analysis such as iron (two phases, austenite and eutectic), the eutectic starts at the end of the liquidus, and continues to the solidus point. In this graphic, the heat energies are separate by a red line. Taking the percent of each area as compared to the total area will give the approximate percentage of each phase.

Minor Arrests

Minor arrests are harder to locate because the small amount of error due to the rounding necessary for higher order derivatives can have a major effect on the starting and ending points of the curve. For this reason, going up to the fifth derivative makes sense. As can be seen in the beta crystal arrest in figure 8, the positive crossing of the 4th - or even better - the 5th derivative is a good point for the start of the arrest, while the negative crossing after the arrest is a good ending point. The positive zero crossing of the 2nd derivative in figure 7 still defines
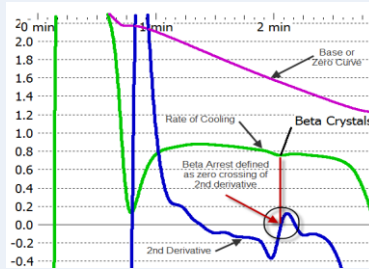

Figure 7. Minor dip in the rate of cooling after liquidus and before eutectic arrest signifies beta phase in Aluminum.
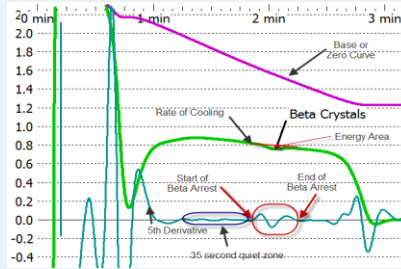

Figure 8. Positive zero cross of 5th derivative marks the start of beta phase, negative zero crossing of same derivative marks end of phase. Note the 30 second quiet zone before the arrest used to calculate the background noise.

the strongest point of the arrest. Integrating between a line connecting the two 5th derivatives and the rate of cooling curve provides a good area for the influence of the beta crystals that are growing in the area of dendritic thickening. This arrest is on the order of 0.4% of total energy from an aluminum heat with about the same (0.4%) iron.

There is one more metric for these small arrests, and that is the significance of the arrest and is taken from statistics. In a noisy electronic environment like a foundry, it is possible to get a false arrest or false zero crossover just due to all the magnetism and electronic energy in the air. The term for this is electronic noise. The arrest can be tested against this noise for statistical significance using a standard sigma test that should be familiar to all quality control personnel in a foundry.

We calculate the standard deviation of the data during a quiet portion of the curve by taking the sum of the square of the distance from zero of a hundred data points from the 5th derivative, and dividing it by 100-1 (n-1 for large sample sizes, n-2 for smaller sample sizes). This is a calculation of the limits of the system to measure. Then we take the strongest value of the 5th derivative during the arrest and divide it by our noise number to solve for X, and we can then say "the arrest is X times or sigma of standard deviation of the noise so we are at 1 sigma, unsure, at 2 sigma, sure or at 3+ sigma very sure that the arrest is real.

Measuring Minor Arrests
1. Start of minor arrest – this is the positive zero crossing of the 5th derivative for independent arrests, or, for major arrests that start during another arrest, it is the negative zero crossing of the 2nd derivative.
2. Arrest point of minor arrest – this is the point of the strongest heat generation during the arrest or the positive zero crossing of the 2nd derivative.
3. End of minor arrest – this is the first negative zero crossing of the 2nd derivative, because there is always another thermal event even if it is only the solidus point, the point where the grain boundary freezes.
4. Arrest energy – this is the integration or the summing of the area bounded by a line connecting the start and end of the arrest, and the rate of cooling curve. Because this is influenced by the size of the sample, this number is divided by the total energy between the zero-curve and the rate of cooling curve to give a percent of the total energy for this arrest.
5. Surety of arrest – the strongest point of the 5th derivative during the arrest divided by the standard deviation of the noise expressed as a sigma value.
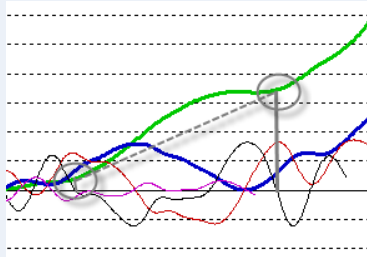
Negative Arrests

Figure 9. This is a shrinkage arrest that appears in iron just after the eutectic point and during the eutectic phase. Negative zero crossings of the 4th derivatives (black) signal the start and stop of the arrest.

Negative or inverse arrests also occur in many metals. When metal solidifies, it gives off the heat that it absorbed during melting. In physics, we call this an exothermic reaction. A negative or inverse arrest is an endothermic reaction, or a process or reaction that absorbs heat. A negative arrest is generated either by shrinkage or by gas formation within the sample. Knowledge of metallurgy and cutting many samples will help identify which arrests we are dealing with. In the iron and aluminum alloys we have dealt with, the gas seems to come out first close to the maximum eutectic arrest, and the shrinkage tends to come out in the latter part of the eutectic arrest.

In figure 9 is a base iron curve at the end of the eutectic arrest. Here the negative 4th derivative zero crossing before and after the arrest seems to be a good delineator for the arrest. The positive 4th derivative zero cross seems to be a good indicator of the strongest point of the negative arrest. Integrate or measure the area between a straight line between the start and end of the arrest and the green curve as a measure of the internal shrinkage. Please note that the shrink propensity of an iron may not be fully measured by this because the sample cup may experience suck-in which does not show up in this kind of arrest. Since this arrest curves upward instead of downward, the direction of movement of the derivatives is reversed from positive to negative.

Measuring Negative Arrests

1. Start of negative Arrest – this is the negative zero crossing of the 4th derivative. This arrest should be limited to the areas of the curve where shrinkage or gas normally appears.
2. Strongest point of negative arrest – this is the point of the strongest heat adsorption during the arrest or the positive zero crossing of the 4nd derivative.
3. End of negative arrest – this is the first negative zero crossing of the 4nd derivative after the strongest point arrest.
4. Area of arrest – this is the area between a straight line drawn across the start and end of the arrest and the rate of cooling curve. This number should be negative when compared to other types of arrests. This energy should then be added back into the total energy of the system and of the phase during which it occurred, as the energy was "stolen" from the total energy by the shrinkage process.
5. Surety of arrest – the strongest point of the 5th derivative during the arrest divided by the standard deviation of the noise expressed as a sigma value.

Measuring the area under the Zero-Curve or Baseline Curve

Finally, there is the problem of the base or zero-curve. This curve is calculated from a point before the start of the first arrest and a point after the solidus point where the cooling rate levels off to a normal "black box" cooling rate. At this point, all heat generation of solidification is over, and all shrinkage effects are over. The curve itself is described by Drs. Sokolowski and Kukus in their definitive paper. When applied to ductile or grey final iron something strange happens: the solidus or End of Freezing point ends up on the opposite side of the zero curve, implying that this arrest is endothermic. Even more curious, samples that show a large area of endothermic arrest at the solidus, do not show shrinkage when the sample is cut! In fact, the samples with shrinkage show low areas for this endothermic area.
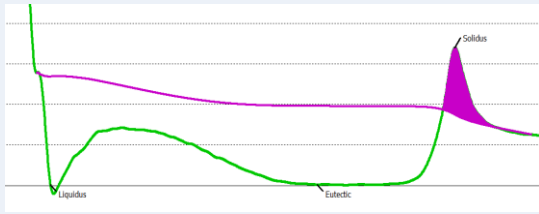
Figure 10. Iron with low actual shrinkage but shows high stress in the solidus arrest.
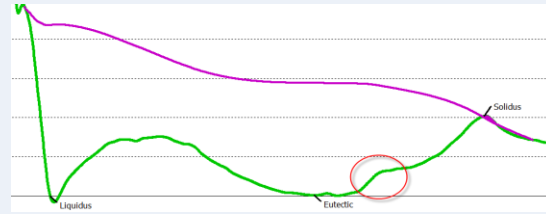

Figure 11. Iron with low stress but with shrinkage arrest (red circle). The shrink relieved the stress in the solidus arrest.

There is an explanation, and that is stress. When metal solidifies, the atoms pack themselves tightly, releasing energy. With stress, the atoms leave spaces and thus don't release all the energy possible. The example in figure 10 had no shrink. The stress area is shown in magenta. The next example in figure 11 did have shrink, in fact, shows a shrink arrest at the end of the eutectic. The area of stress is almost non-existent in the sample with shrink showing that the shrinkage relived almost all the stress.
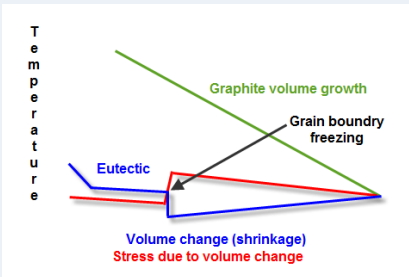

Figure 12. While the graphite growth starts at the eutectic and continues through freezing, it does not keep pace with the sudden volume change at solidus (grain boundary freezing).

The explanation for this is that the graphite growth does not match the iron contraction until sometime after the solidus temperature has been passed. This puts about a 1% volume loss in the casting at solidus. At that point, one or more factors make up for that loss. Stress is the most common and will generally account for most of the volume loss in a "sound" casting. Microporosity is another form of shrinkage that will relieve some stress and occurs when the casting walls are strong. Large shrinkage, which is picked up as a shrink arrest on the curve, is another way the volume loss is made up.

And finally, if the walls are thin and not strong enough due to a hot spot, the casting wall may be sucked in to relieve the stress from the volume loss. Later, as the graphite growth catches up with the volume loss, the hydrostatic pressure can remove the stress, and possibly collapse some of the finer shrink. If not, then the overall casting size may grow slightly, leaving the foundryman with a difficult question: "Is the casting that is oversized and has massive shrink due to soft molds or late graphite growth?" This is not to say there are not also gating problems that affect shrinkage, but that is not the subject of this paper.

Conclusion

These tools should allow a more thorough investigation of the thermal analysis of metals. They do not tell us what each arrest is. That is the undertaking of metallurgists with other tools such as phase diagrams, microscopes, spectrometers, etc. Further, the rates of the reactions can be explored and equations calculated to estimate grain/cell counts, dendritic arm spacing, or, in ductile iron, nodule count.

The noise calculation, if done during the period of the eutectic arrest of ductile iron, acts as a predictor of vermicular graphite, and, if over the same period in grey iron, of undesirable flake shapes. The noise calculation in these graphite producing arrests needs to be done when the iron is the quietest, which appears to be at the start of the eutectic. There will be more on this later when we look at this graphite noise signature next month.

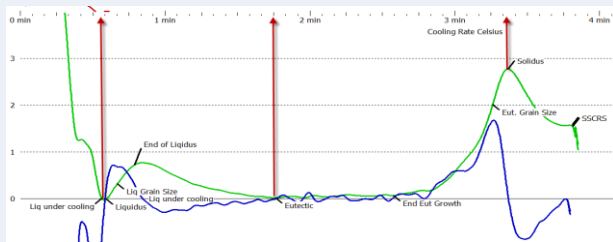**Appendix A – short poured cups and low pouring temperatures can affect the thermal analysis**

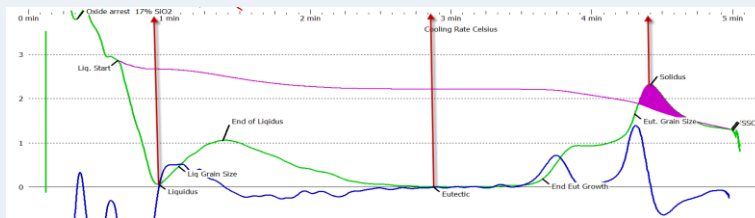Figure 12 Shorter cooling time inhibits start of liquidus arrest

Occasionally we miss the start of the zero-curve on a test. It appears from the graphs below to be caused by not enough iron in the cup which then increases the speed the iron cools off. In the graph in figure 13 with a zero curve (magenta), the liquidus occurred at 1 minute, and the solidus occurred at 4 minutes, 20 seconds. In the graph in figure 12 poured on the same day in the same foundry, the liquidus occurred at 35 seconds and the solidus at 3 minutes 20 seconds.


Figure 13 Longer cooling time detects liquidus start for zero-curve

This shift could be caused by either colder iron or less iron in the cup. Since the max temperature was 1244˚C in the second graph, and was 1344˚C in the second graph, it is hard to tell which the cause was. Personally, since the superheat in the figure 12 curve was 105˚C, I suspect that the temperature was adequate, and that the problem was that too little iron was added to the cup in figure 12.

The conclusion is that the graph in figure 12 shows a shorter analysis time due to either less metal in the cup or lower temperature. It then has no start of liquidus point due to extreme initial rate of cooling. Note the curve bending at 25 seconds in figure 12 is too low to be a start of liquidus. The rate of cooling at the start of liquidus always seems to be higher than the end of liquidus point (highest point between liquidus and eutectic on the rate of cooling curve. The graphs have been aligned by the time scale to better illustrate the point.

Hence a better sample with a longer analysis time is produced when a sufficient amount of metal or more temperature is used in sampling. The large amounts of oxides in this example are not helpful and could possibly interfere, but in this case we do have a reasonable start of liquidus at about 2.5 degrees per second cooling rate.

**Appendix B – Growth Temperature Arrest explanation and definition**
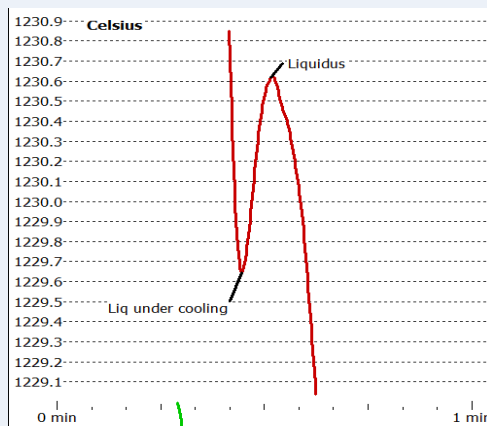
Example of growth temperature lacking flatness

This liquidus from figure 1 is shown on a different scale to show that there was no flatness at the liquidus point. The temperature reaches a maximum and then immediately goes back down. Hence this is the growth liquidus, not the true liquidus. If the metal had reheated to the true liquidus point, it would have hit a "ceiling" above which it couldn't go without remelting. It would then bump against that ceiling, making it flat at the top. That would "prove" that the reheating reached the true liquidus.

In the second graph, the eutectic of this arrest stays flat for about 10 seconds, proving that it has reached its maximum temperature and is the true arrest temperature. A useable definition of a ceiling is for the arrest to remain within 1/10˚C of the maximum temperature for more than 10 readings, or in the case of MeltLab, for about 1 second.
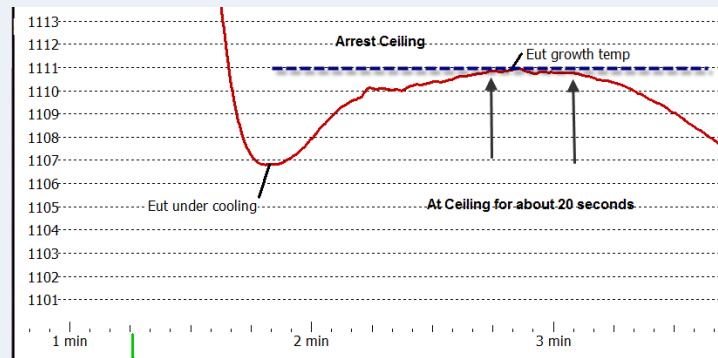
Example of a ceiling in an arrest that lasted for about 20 seconds.

Appendix C – Steady state cooling rate of a solid or SSCRS

Toward the end of the thermal analysis of a cup sample, the cooling rate approaches what is called black box cooling. This is where no further reactions are occurring, and the temperature decreases due only to radiation loss (black box radiation) in a form that looks like a logarithmic function. This point is used by MeltLab for the right side anchor of the zero-curve. The definition for this point is where the 4th derivative has a positive zero crossing after the solidus arrest and where the 2nd derivative is greater than -0.01˚C per second[2]. The reason for this complex rule is that this area of the graph in iron is subject to some abnormalities, due to the sand cup beginning to disintegrate. Sand falling off of the cup momentarily increases the rate of cooling and should be deemed an artifact and not an event.

Appendix D – Zero crossings

Each temperature/derivative measurement can be compared with the next measurement to see if the sign of the value changed. Going from -0.001 to 0.003 implies that we have crossed zero in a *positive* direction. Likewise moving from 0.000 to -0.002 implies that we have crossed zero in a *negative* direction. Finding these crossover points is the first step in locating the arrest points.

Appendix E – translating percent heat energy into percent volume or chemistry

While it might be nice to calculate chemistry from the area of an arrest, it is theoretically difficult. We would also need the specific heat and the specific density of these phases at the temperature involved, and those values just do not exist in literature. Indeed, finding them through research would also be very difficult.

But being practical engineers, it is easy enough to say that we can measure surface area of a phase by microscope and/or image analysis, and we can measure chemistry by spectrometer or atomic adsorption techniques and calculate a correction factor that will prove satisfactory. So we take the measured chemistry divided by the measured percent of the heat energy that phase represents, and come up with the correction factor. We can do likewise with the percent surface area to get percent volume, though going from two dimensions to three introduces a degree of uncertainty in the transition. So far our tests on the factor *Percent FE/Beta Energy* comes out very close to 1 as does the *copper energy/percent copper* factor in aluminum. The magnesium silicide to magnesium also appears reasonably close to 1.