Metrics of Thermal Analysis part 2 – Measuring Inoculation

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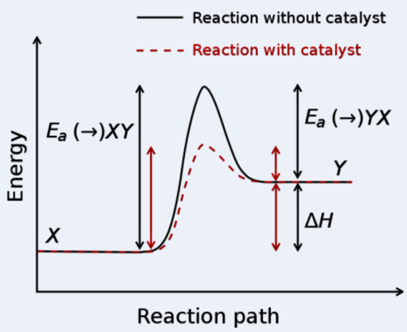
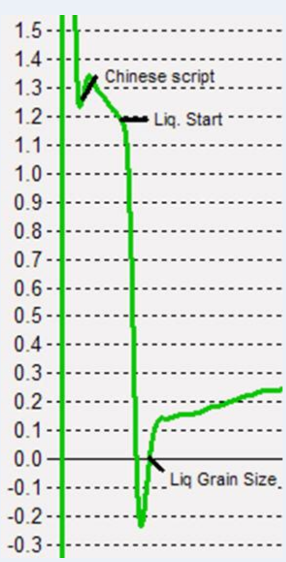


In this scope, the term "inoculate" means to add a material (catalyst) to a molten metal to increase the cell count and reduce the under-cooling of a phase in the metal. In gray iron, we inoculate to promote more A/B flake and decrease undercooling which leads to D and E flake. In ductile iron, we inoculate to promote the formation of late graphite, increase nodule count and prevent carbides. In hypoeutectic aluminum we inoculate to promote smaller dendrites, and prevent undercooling and hot tearing. In hypereutectic aluminum we inoculate to promote the formation of smaller silicon particles. There are many other metals that also use various materials to promote cell count and prevent undercooling. This article discusses how all these various methods may be measured and quantified.

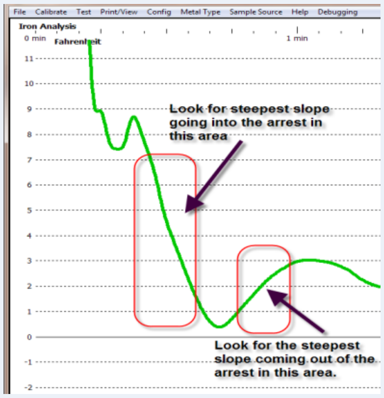
Crystallization produces heat at a metal changes from liquid to solid. But crystallization usually requires a little extra energy to get it started. Normally the metal undercools until the driving energy is enough to provide this extra energy. Inoculants, as shown in the diagram above, provide a means of reducing the extra energy required, generally by providing or reacting with other material in the metal to provide a crystal surface on which the main crystallize growth can begin. By providing a lot of these sites, the metal changes it's characteristics and increases it's cell count by orders of magnitude.



Measuring this effect is usually done in three ways. First, some metals, such as ductile iron, will show distinct undercooling. Second, other, metals such as highly inoculated hypo-aluminum, will show a higher start of liquidus. And third, the speed of crystallization is generally increased due to the greater surface area, and the shorter diffusion paths of highly inoculated metals. We are going to look at each method and find how they can be applied to different metals to measure microstructure effects related to cell sizes.

Undercooling is when the metal drops below the crystal growing temperature. As can be seen to the left, the aluminum undercooled by 0.23 degrees (-0.23) before the reaction took off. Often it will then heat back up (recalesence) as the crystal formation rapidly releases heat. This temperature though can never go higher than the true liquidus. Dr. Backerud first used the term "growth temperature" for the highest temperature reached in a crystallization reaction.

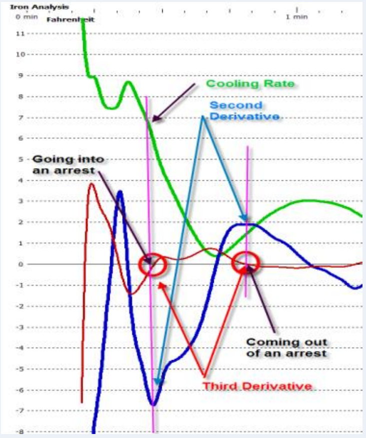
Many years ago Nick Walker and others designed an instrument: AluDelta, to measure the recalesence (reheating) in aluminum. This is a small effect seldom exceeding 2 degrees C. The research, done back in the 1960's[1], compared the grain size (proportional to 1/inoculation cell count[2]) on a chilled aluminum sample with the recalesence but was limited in a number of ways. First the correlation was good for higher numbers but got a bit fuzzy as the recalesence approached zero, and second, the method itself had no way of accounting for when the rate of cooling did not reach zero (i.e. no recalesence) other than to post the value 6666 for a near zero derivative or 9999 for a non-positive derivative such as in the case shown below. In fact, very highly inoculated aluminums show a rate of cooling that never goes below 0.2 degrees C. This limitation could not tell the user how much over inoculated the metal was and therefore how much to cut back on the inoculation.



Likewise grey iron and ductile iron will often see the eutectic arrest undercool. With good levels of inoculation, the undercooling is slight. If the undercooling is controlled, then the degree of chill, and the bad effects of over inoculation could be controlled. In a previous paper, I documented how the undercooling in thermal analysis can be used as a substitute for chill wedges will fewer operator influences.

To recap: Inoculation points turn into dendrites or crystals depending on the alloy. Inoculants work by providing a catalyst or surface on which the desired crystalline structure can start growing, thus reducing the energy of activation for the crystal to grow. In general, in ordered to promote a finer structure with better metallurgical properties, we want to reduce the amount of energy (undercooling) needed to start growth, and to set up a high number of growth sites throughout the metal.

The key is that in thermal analysis, a high inoculation cell count material releases energy faster than a low cell count material for a couple of reasons. First the higher number of inoculation cells has more surface area for the reactions to take place, and second, the length of the diffusion path of the material forming the cells is shorter with higher cell counts.



So in thermal analysis we look for not just how much the cooling rate changes, but how fast the cooling rate changes. Since the cooling rate is 1/1st derivative, the rate of change or slope of the cooling curve (**Green**) is the second derivative (**Blue**). The highest rates of change will be marked by the 3rd derivative (**Red**) crossing zero.

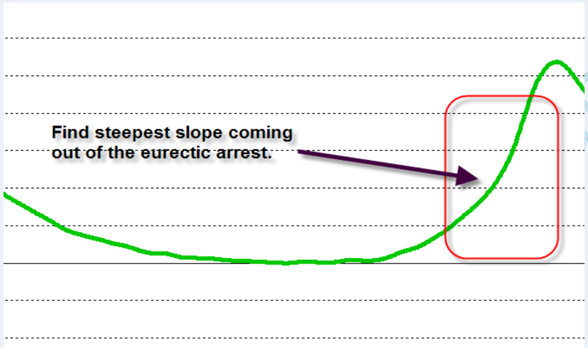
There are then two points in each arrest that indicate the cell count: the point defined by the third derivative going into the arrest, and the same point going out of the arrest. The point going out of the arrest may need some explanation. Crystallization stops when the reaction has used up all

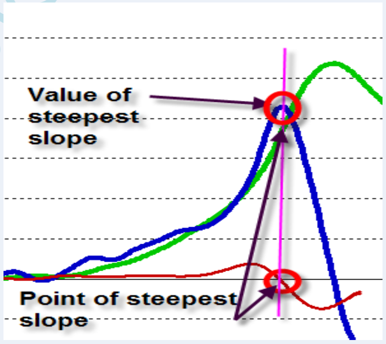
[1] *Assessment of Grain Refinement and Modification of Al-Si Foundry Alloys by Thermal Analysis* by D. Apelian, G.K. Sigworth, K.R. Whaler, AFS Transactions 84-161, 1984.

of its fuel. A high cell count means that the distance between cells is shorter, and, in effect the fuel makes it to the cell quicker. Like a campfire made of twigs, it quickly consumes its fuel and goes out, where a campfire made of larger logs burns long and slowly.

From the example above, the point going into the arrest has a value of -6.7˚/ second^2 (blue line) where as the point going out of the arrest has a 1.6˚/ second^2 value. The question is which of the two arrests is more consistent if we are going to try to use it as a measure of cell count. The answer is surprisingly the second one. The first one is stronger (absolute value) because the crystallization arrest begins on the outside of the sample and moves in toward the thermal couple. Some of the heat of the far away reaction adds to the heat change occurring in the near vicinity of the thermal couple and slows the cooling rate. By the time the second point (going away from the arrest) occurs, there is no external influence on the curve. So for reliability the second point seems better.

Finally, in ductile iron, we have an unusual "cell count" to measure: the graphite nodule count. Again the basic physical principles work, though the end of the eutectic reaction in ductile can be confused with carbides and shrinkage arrests masking the steepest slope. Still for most applications making good castings, the final slope before the end of freezing point (solidus) is a good indication of the diffusion distance between nodules which relates directly to the nodule count.





That value is the steepest slope of the cooling rate, or the maximum 2nd derivative value (blue) which the computer finds when the 3rd derivative (red) crosses zero.

C omment from Dr. J.Jorstat "You refer in the article to inoculation in hypoeutectic aluminum alloys to promote smaller "dendrites", and throughout the article you refer to "cell count". We in fact inoculate to nucleate dendrites, which grow into grains -- each dendrite becomes a single grain, so the more initiation sites, the smaller the grains, and in the world of aluminum castings that is referred to as "grain refinement" (you don't seem to use that term). And cell count or cell size in the world of aluminum castings is used to indicate the size of sub-grain cells -- the most common terminology is SDAS -- secondary dendrite arm spacing -- the average distance from the center of one secondary dendrite arm to the center of its neighbor. SDAS is a function of cooling rate during solidification and is not controlled by nucleation. Coarse and fine grains (refined or unrefined) can have exactly the same SDAS. You seem to be using the term cell count as an indicator of grain size whereas aluminum foundries reading your article will perhaps be led to believe that MeltLab is measuring SDAS."

Reply: Well said. The amount of "grain refinement" is what is being measured in hypoeutectic aluminum-silicon alloys. We try in thermal analysis to maintain the same cooling rate from sample to sample. Although I have never seen a definition of the overall cooling rate, I do know that the standard practice for phase diagram research is about 1˚C per second. Personally, I use the cooling rate of the start of liquidus point as the best approximation of the overall cooling rate. The first example here shows 1.2˚ C per second for the "start of liquidus" point. (The second example is from iron and a sand cup.) Perhaps this value should be added to the list of data generated by MeltLab so foundries can be more consistent in their evaluations. When using the Pechiney type cup for aluminum evaluation, the sample size seems to be the controlling factor in the overall cooling rate. Sand cups generally do not allow the measurement of the start of liquidus in aluminum alloys due to the quenching effect of the unheated cup. Even iron alloys require a lot of superheat to clearly define the "start of liquidus" point well. BTW, the start of liquidus point is also the beginning of the "zero curve" used for integrating the different phases – more on that later.