

Ductile Iron Microstructure by Thermal Analysis

One promising new technology is the rapid classification of microstructure by thermo analysis. Current technology consists of either pouring a sample with two ears on it for micro analysis or creating a micro lug in the runner system of a mold and digging the lug out for grinding and polishing. Both techniques are “after the fact” or as we often say, “post mortem” since a bad result results in scrapping already poured castings.

For a while there has been an analysis method by NovaCast, and now cloned by Elkem to analysis a treated ductile iron sample for the propensity toward shrinkage. But there is so much more that can be learned though thermo analysis.

NovaCast identified several characteristics of the thermal curve as pertaining to good castings. First they wanted to see a quick rise in the eutectic temperature as compared to the length of the eutectic arrest (T_2 to T_3 Ratio). This depended on good nodule count and is soundly based in metallurgy.

Second, they looked for a sharp drop in temperature at the end of the eutectic. This shows up as a strong dip in the first derivative, or a sharp peak in the cooling rate. This arrest is due to a large stress in the grain boundaries. The lack of this stress means that shrinkage has relieved the stresses. The stresses may affect fatigue life, but no one has investigated that aspect. For sure, shrinkage will also greatly reduce fatigue life.

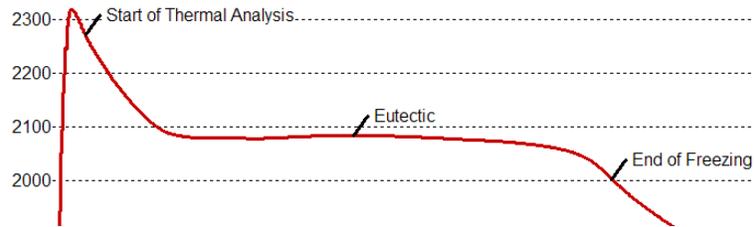
With some previously published information from MeltLab introducing the concept of the slope of the temperature fall off after eutectic as an indicator of grain size, Elkem has adopted reporting that slope.

Additional features in Thermal Analysis

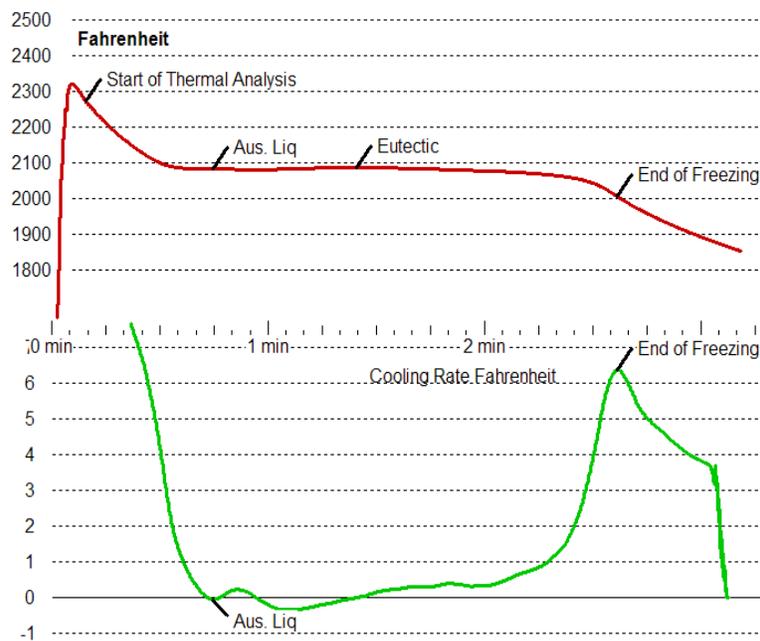
The first concept is that not all ductile foundries need the same kind of ductile iron to make quality castings. The treatments by NovaCast and Elkem are aimed at the average foundry making thinner section castings and do not discriminate between hypo-eutectic, eutectic, and hyper-eutectic irons. The published examples all appear as eutectic curves, though closer examination is needed to pick out the near eutectic curves.

Let's start with some definitions of terminology. The term “eutectic” means both lowest melting point, and single arrest. Many may assume that an eutectic curve (single arrest) corresponds with the Iron Carbon phase diagram C.E. of 4.33. This is not always so for two reasons: first, magnesium suppresses the formation of graphite which delays the formation of graphite and allows an austenite liquidus to form higher than 4.33. Second, the instrumentation used by both NovaCast and by Elkem cannot always find an austenitic arrest hidden in a eutectic arrest. Nor do they spot the small graphitic liquidus arrests of extremely hyper-eutectic iron.

Here is a typical “eutectic curve” with what appears to be a single arrest. The lack of resolution hides the austenite liquidus present.



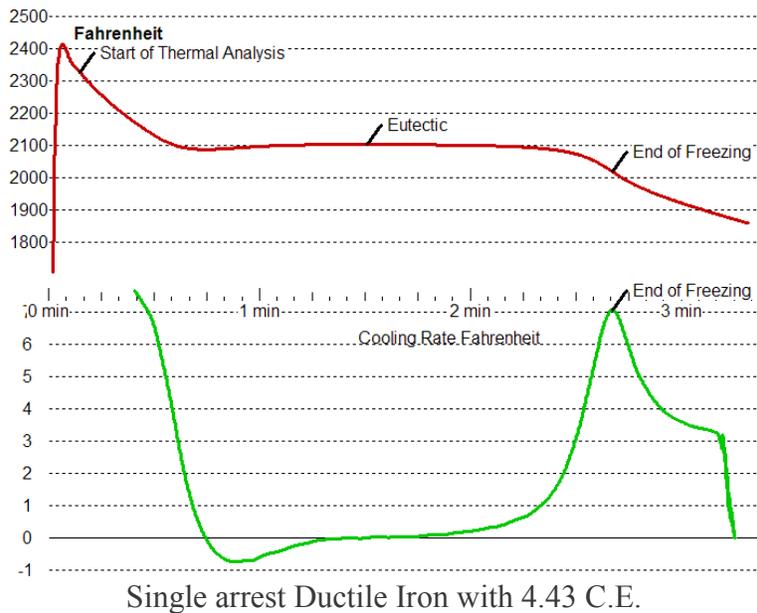
By showing the rate of cooling curve below, the austenite liquidus is seen before the general eutectic arrest.



Actually it is a hyper-eutectic at 4.49C.E.
but with an austenitic liquidus due to magnesium

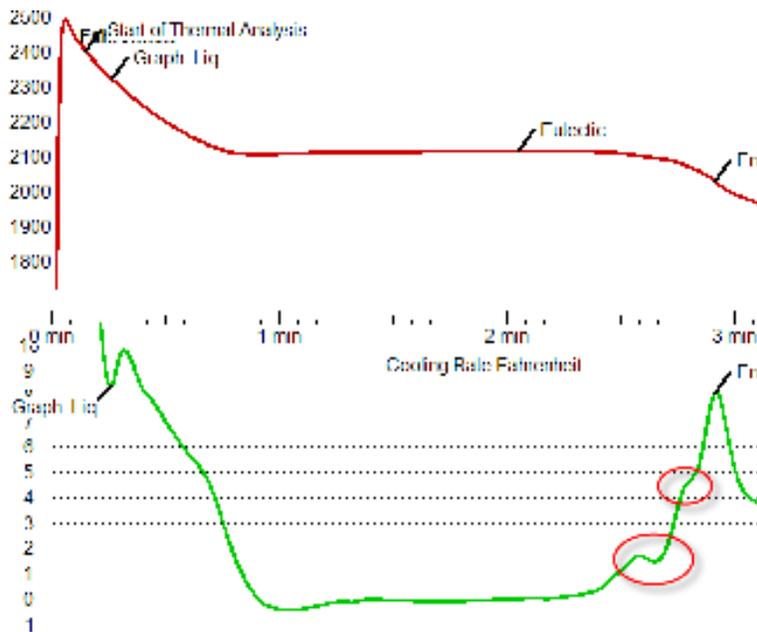
The above curve without and with cooling rate demonstrates the need for a close look at the cooling rate to pick up the small but significant austenitic arrest. Nodularity is not as good as can be had as can be seen by the fine roughness in the green curve during eutectic, and there is an indication of shrinkage at 1:50 minutes into the sample. More on this later.

The following curve is a true eutectic curve, even though the C.E. is 4.43%.



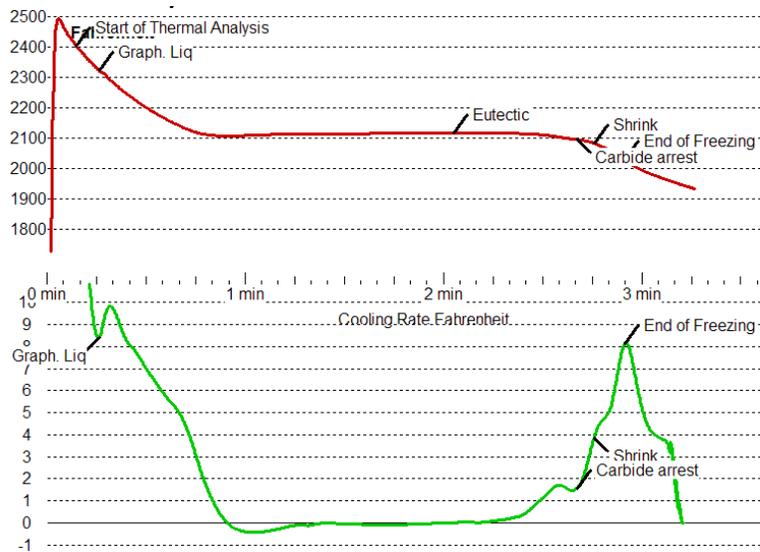
This kind of iron is ideal for normal section castings and provides good shrink control for reasons to be explained later. Nodularity is quite good in this sample as can be seen by the smoothness of the green curve.

The final type of curve is a hyper-eutectic arrest with a graphitic liquidus, and often with an austenitic liquidus as well.



Hyper-eutectic iron with graphitic arrest at 4.60% C.E. and other problems

The graphitic arrest is quite weak, but shows up as a clear arrest in the cooling rate. Looking only at the red temperature curve, it would be easy to miss. But look at the fall out. We have a good smooth green curve during the eutectic indicating good nodule shape, but we have two very bad arrests between eutectic and end of freezing. The first arrest at 2:30 minutes into the analysis is exothermic or heat producing. At this point in the curve, that indicates a D or E flake formation commonly referred to as carbides. The second smaller arrest is endothermic or heat adsorbing. This is actually shrinkage forming in the sample.



Hyper-eutectic iron with graphitic arrest at 4.60% C.E. showing carbide arrest and shrink

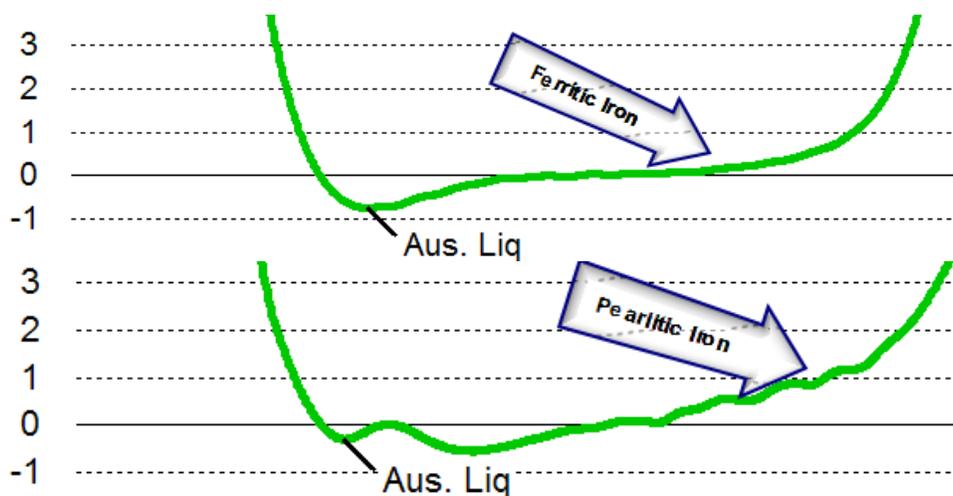
Shrink in ductile iron thermo analysis

In steel, the shrinkage rule is 10%. This means that the pattern will be designed for all dimensions to be 10% over stated so that when the casting cools, it will have shrunk to near the right size. In ductile iron, graphite occupies between 9 and 11% of the volume, while in liquid ductile iron, carbon occupies no volume. The miracle of ductile iron is then that graphite grows in the solidifying material to almost perfectly match the shrinkage. The key word is “almost”. If we get enough graphite to come out of the liquid at the right time, we produce sound castings. If not, we find shrinkage in our castings.

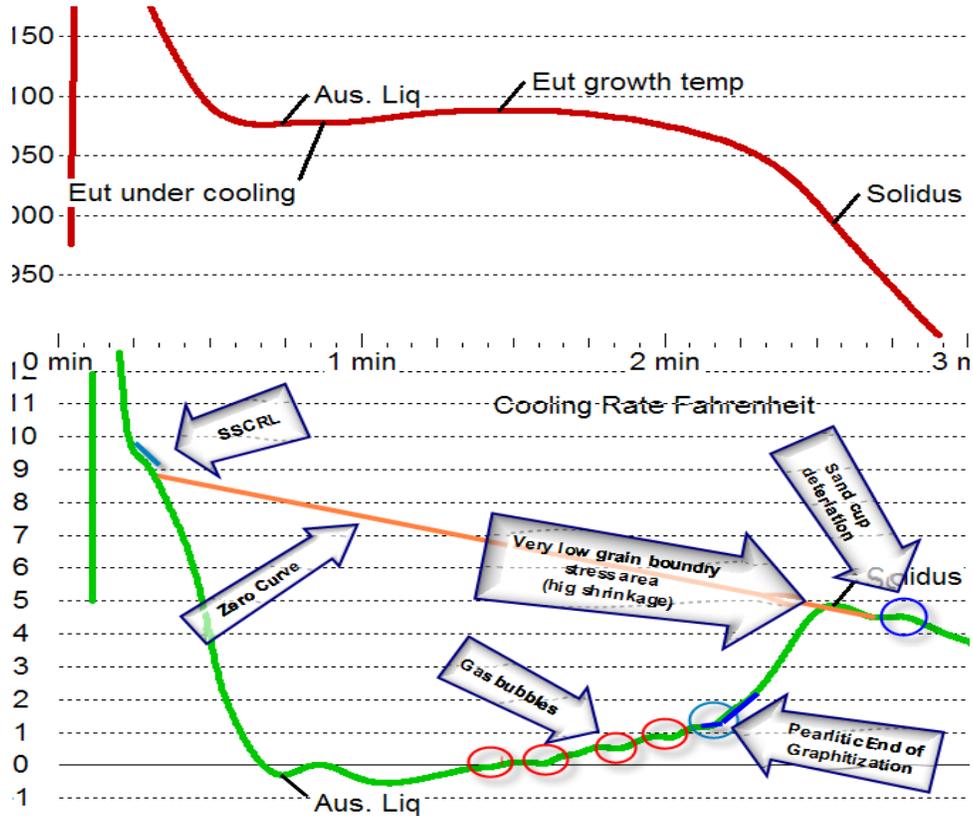
The purpose of the gating system is to feed liquid into the cavity as the liquid cools. Liquid iron at 2200 degrees F has less volume per pound than liquid iron at 2300 degrees F. We want the gates to freeze off before the graphite starts to grow in the mold cavity. This traps the increase in volume inside the casting; instead of pushing iron back out into the runner system and making solid risers. This works best if no significant amount of graphite comes out in the liquid. Obviously if you do have graphite forming in the liquid you would expect to find a bimodal distribution in your nodule sizes. There is some discussion if the larger graphite can also grow in the early austenite arrest and so give rise to bimodal distribution.

The effect of Pearlite on Shrinkage and the thermal analysis

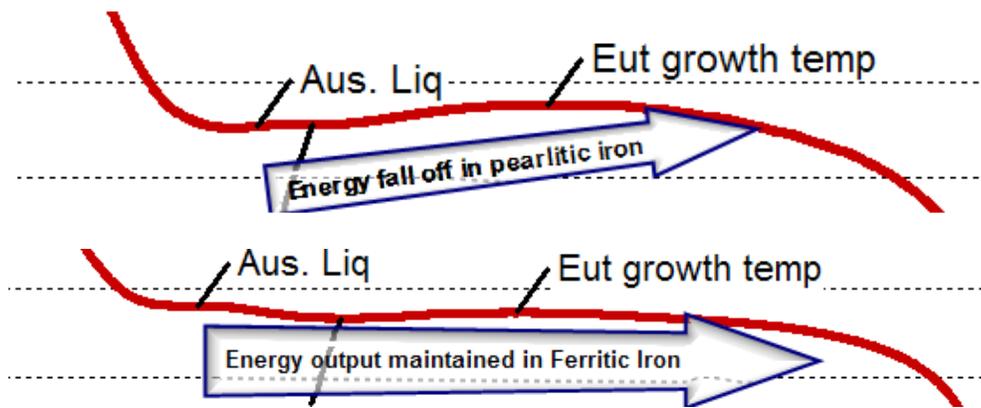
Second, some carbon does remain in the iron after solidification. Some is in the obvious form of carbides or pearlite, but some remains in solution below microscopic detection. This is proven by the effect of heat treating causing an increase in graphite volume even in fully ferritic irons. Increased nodule counts contribute strongly to more complete graphitization. And obviously carbide stabilizers decrease graphitization. In the thermo analysis curve, the prolonged eutectic plateau is a good indicator of the degree of graphitization, and its counter: an early end of the plateau, a good indication of pearlite content.



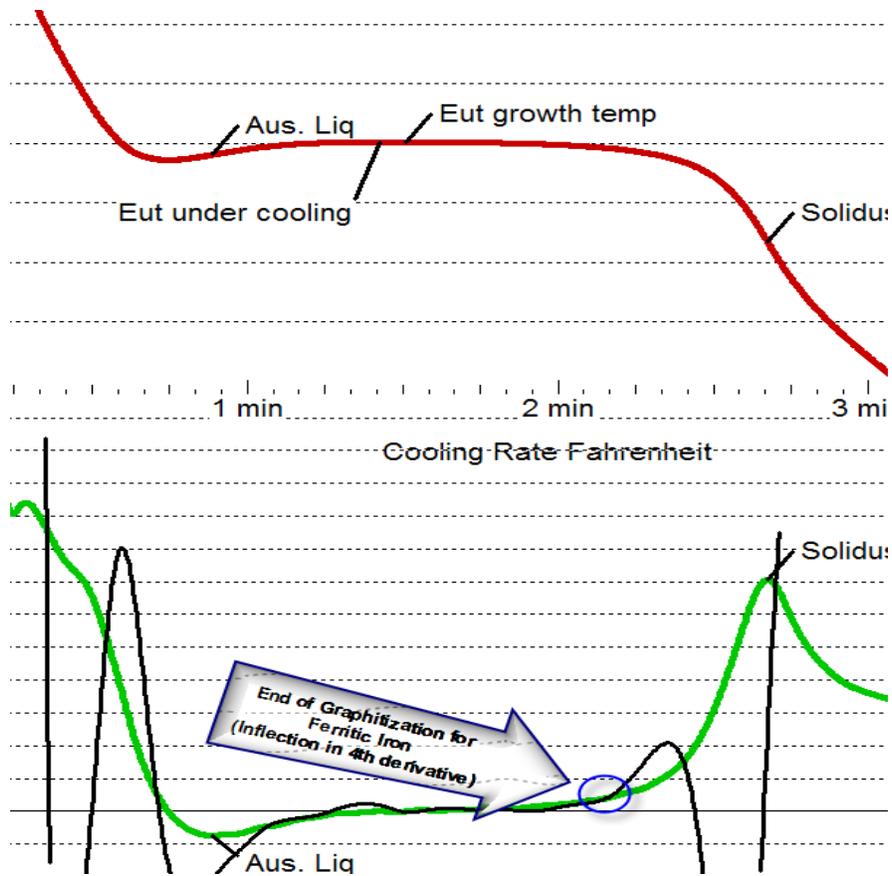
Here are two cooling rates, the top is ferritic iron, and the bottom is pearlitic iron. The energy production of the top curve is significantly greater toward the end of the eutectic arrest.



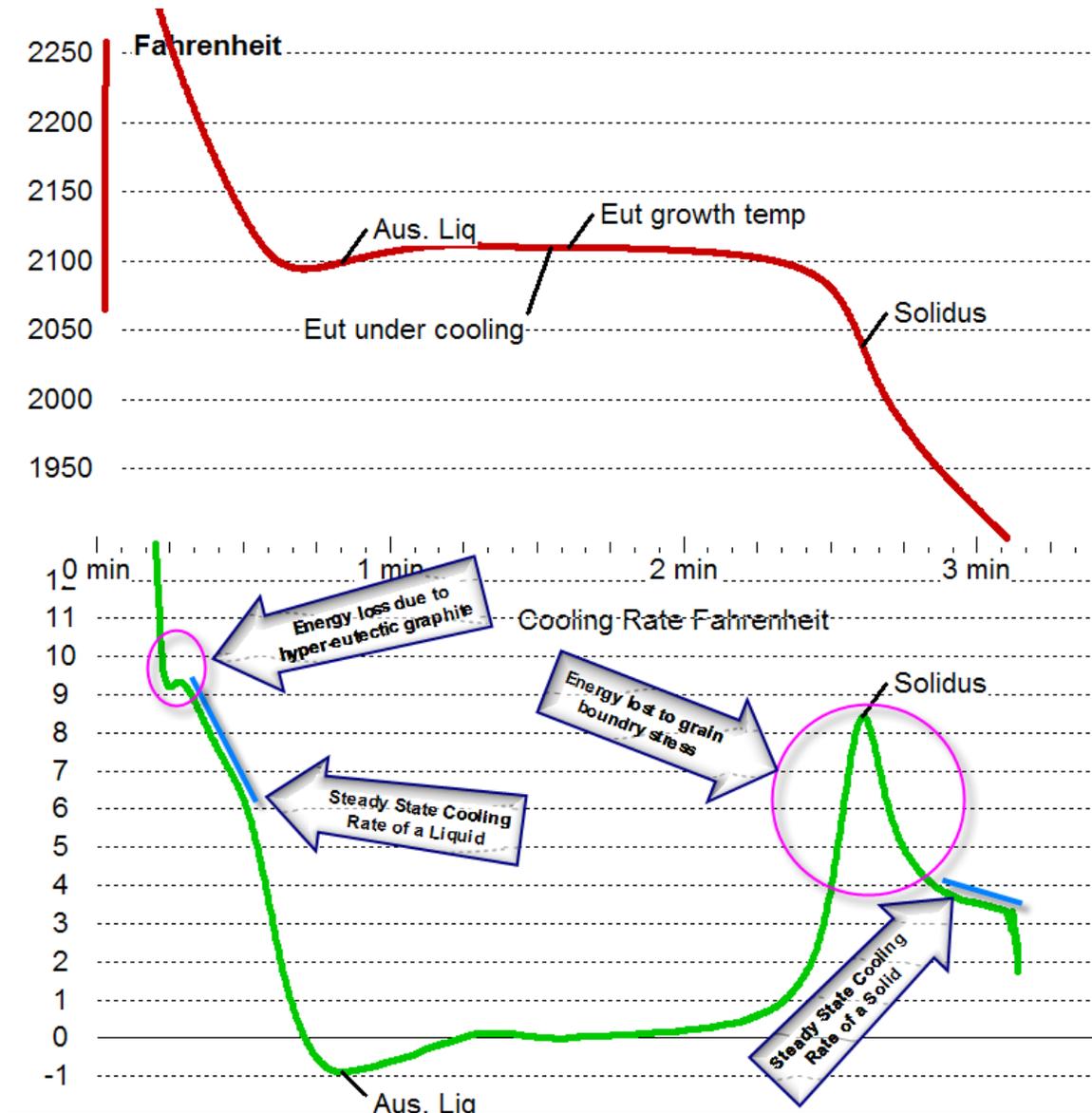
In this example of an 80% pearlite, the End of Graphitization is lifted up to about 1.2 degrees per second rate of cooling. Not near as much graphite came out of this iron. Please remember that the carbon is still all in the matrix, the pearlite does not form until 1400-1450 F. But because it is still in the matrix as a form of austenite, it's energy has not yet been released.



The above two examples show the temperature curve of a pearlitic curve (top) and a ferritic curve (bottom).

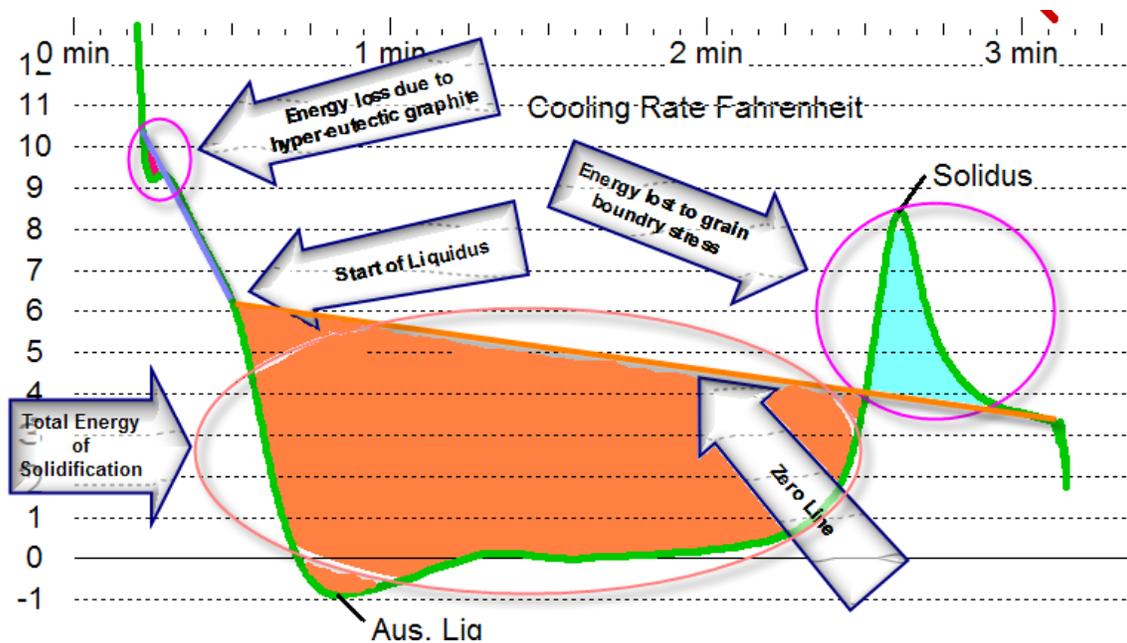


This is an example of Ferrite ductile (<10% pearlite). The 4th derivative is shown in black so you can see the bend associated with the end of graphitization. This point is at about 0.4 degrees per second rate of cooling, so the material has been able to maintain a much flatter eutectic due to higher energy production. Of course the ferritic iron also has higher nodule count, you don't want to over inoculate pearlitic iron. It gets soft.



In this ductile sample, I would like to introduce the Steady State Cooling Rate concept. When no crystallizations or solid state transformations are occurring, then the metal loses heat at a steady, mathematically describable rate due most exclusively to radiation and conduction. Here I have drawn straight lines to represent the SSCR of the iron liquid (SSCRL), and the iron solid (SSCRS). The lines are slightly offset so that you can see how they parallel the actual readings. In reality the lines show a slight bend and are logarithmic. The reason for the different slopes is that conductivity and radiation rates change with structure.

The usefulness of this concept is that these lines can serve as a boundary or delimiter for energy production. Combined together, they define what in the literature is called the zero line. Here is an example of how those lines extend to make energy boundaries.



The start of Liquidus is where the curve breaks away from the SSCRL cooling rate and begins to produce heat. Linking this with the SSCRS gives us the upper boundary for calculating the energy of solidification, as well as a lower boundary to calculate the energy adsorbed by the grain boundary solidification. These are very important measurements for calculating the quality of the ductile iron. Knowing the total energy of solidification allows us to ratio any arrest such as carbides or shrinkage against the total energy, and come up with a percentage of energy for each type of arrest. While the energy for each type of reaction may differ (different specific heats), knowing that one sample had carbides of 1% of the total energy vs. one with 0.1% of the total energy allows us to understand the severity of the problem.

Understanding where the lines come from, let's look at the meaning of the area under the Solidus point known as the grain boundary stress area (GBSA). This is an endothermic reaction that sucks up energy due to disorder (stress) in the grain boundaries between crystals. Sometimes it is quite large, sometimes it is quite small. Nova Cast has used the height of the point as a shrink indicator based on their studies, and for good reasons.

There should always be stress in the grain boundaries after solidification. In the long term, heat treating removes these stresses by increasing the amount of graphite present. But in the short term, there is too little iron for too much volume and there is only one way to reduce the stress – shrinkage. The shrinkage may take the form of a suck-in on the top or sides of the thermal analysis cup, or by forming actual shrinkage inside the casting. The shrinkage shows up on the thermal analysis curve, the suck-in does not.

So a quick estimate of this stress is the height of the Solidus point. But since that can vary with how well the cup is filled, a better estimate can be the area between the Rate of Cooling curve and the zero line ratio against the total energy of solidification.

In summary, shrinkage has many causes, graphitic liquids' can remove significant amounts of carbon, the carbon/C.E. content may be too low, inoculation can alter when and how much of the graphite comes out. Pearlitic irons are designed to retain from 0.3 to 0.6% carbon in the matrix which later comes out as between 40 and 80% pearlite. (40% times 0.8 Carbon in 100% pearlite equals 0.32% retained carbon.)

Statement of thanks

(With a slight nod to Bill O'Reilly for an attitude check)

It is customary in research papers to list a bibliography of all references searched. While this is a good practice and recommended and even required by those who pass judgment on a paper's worthiness, I find it difficult to recommend most research on this subject as they contain so many errors and misconceptions. While a good grounding in metallurgy is necessary to understand some of these concepts, and history is an interesting field, the study of disease and astronomy before the age of the invention of the optical lens by Galileo produced mostly useless information.

In metallurgical thermo analysis, the lack of clear and sharp derivatives made analysis only guesswork. A paper by a studied researcher mentioned the elusive graphite arrest. It is visible in DTA but not in normal thermo analysis. Therefore many researchers do not believe that you can produce graphite in a liquid in normal foundry iron. But you can see it with the modern tools of MeltLab.

My Heroes

My thanks go out to Jeff Burk, Dick Heine and Bill Shaw for first interesting me in the possibilities of TA, to Carl Loper for introducing me to grain boundary freezing, to Toban xxx for an interesting discussion on graphitization of ferritic and pearlitic irons. And finally to Doru Stephenescu for discussions on the Zero curve.

Now for the Pinhead section

My undying gratitude goes to ElectroNite for copying MeltLab's Solidus Point and for their continuing hatred and putdowns of MeltLab that have only encouraged me to embarrass them further. Last overheard from them: "what are we going to do about those people in Virginia?"

My undying gratitude goes to greedy Minco and OCC for selling our products to a few customers while secretly having programmers attempt to duplicate MeltLab. Sorry those products failed.

And finally my fond farewell to NovaCast who through kickbacks (up to 20% according to one Metallurgist) and other financial incentives, tried to sell an overpriced box (40k+). They exchanged heavy advertising in the DIS for preferred treatment in making multiple presentations that included nothing but more advertising. They also succeeded in hiring away a technical writer/researcher from us to get at MeltLab technology. Their attempt, with investor money, to control the market for ductile thermo analysis is now coming to an end. Their promises to investors were just smoke and mirrors. Now that Elkem Metals (a good company with value in its products) has produced an ATAS Light product (there is a lawsuit over that), and with the introduction of MeltLab for Ductile, the overpriced ATAS product will soon, if not already, be history.