Ductile Iron Revisited – a conversation

Recently I participated in the ICRI meeting in St. Cloud, MN along with NovaCast. As many of you know, NovaCast brought out its ATAS system (A Thermal Analysis System) many years ago and using correlation analysis, and a large contribution from the government of Norway, created a software package to determine if you have final iron good enough to make good ductile iron. The system was custom fitted to the application with an engineer taking a week or more to study your results, your micros and your physical tests to determine the proper characteristics of your thermal analysis curves to make good iron.

For that you paid an estimated $40,000 per instrument (not sure how deep their discounts go). Their pricing is kept confidential so we are using only hearsay, but we can safely say it is the second-highest priced system in the market, with the CGI system from Sintercast being the highest priced Thermal Analysis system offered to foundries. Sintercast systems are for CGI only and go from small $70,000 systems up to over a million (Ford Brazil). For that you a very fancy box, and on the high end, a live-in technician and plc control

In this market, MeltLab is priced as the lowest cost Ductile system running at about $18,000 for a single station, with multiple stations running slightly more, or as a $5,000 add-on (additional station included) to an existing base iron MeltLab system.

While we applaud NovaCast for their slick advertising and screen presentation, MeltLab does include all the pertinent features needed to control your final ductile iron. So let's review those.

The Freezing Mode

The first, and most important factor to controlling shrinkage is your carbon equalivant and hence your solidification mode. Your iron can have one of four modes of solidification: hypo-eutectic, eutectic, hyper-eutectic, and a strange mode that is both hyper and hypo-eutectic. MeltLab identifies all four modes. Before discussing each mode, let me explain why I use the term "mode". There are two different definitions for the term eutectic in metallurgy. The first is the chemistry of the lowest theoretical melting point. Hence you can buy eutectic solder, a solder with the combination of lead and tin that has the lowest melting point. The second definition is the one I want to use here. A eutectic iron is one that has a single freezing arrest – a single mode of freezing. If you closely observe thermal analysis curves, you will find that ductile iron has a single freezing arrest from a C.E. of 4.33 through a C.E. of over 4.55 and maybe as high as 4.60. Text books suggest that "magnesium suppresses the growth of graphite". That may be the cause, or it might be the lack of dissolved oxygen due to the presence of magnesium and calcium. There is still a good deal of research to be done in this area.

Hypo-eutectic mode iron (below a 4.3 C.E.) is used for heavy section castings to prevent carbon flotation. This is not the kind of carbon flotation called kish, but rather the kind of flotation deep inside of the casting, when graphite forms in the remaining liquid and starts to rise up, leaving carbon-starved liquid metal below. The signature of this problem is shrinkage below a carbon rich layer of iron in a thick section. Hypo-eutectic iron forms dendrites in the iron that blocks graphite movement. The dendrites also can choke off smaller gates and cause issues there, so the gates are usually large, as are the risers in hypo-eutectic irons. Due to the growth of dendrites, hypo-eutectic irons develop strong casting walls early on and can better resist wall movement, both in (suck-in) and outward movement.

Hyper-eutectic mode (method of freezing, not chemistry) irons are generally bad news for any kind of ductile castings. In this mode of freezing, graphite forms in the free flowing liquid inside a casting. The formation of graphite expands the volume of the casting and, since in the smaller castings the gates are generally still open, pushes iron back into the risers to give solid risers. The result is that the casting does not have enough late graphite to prevent shrinkage. Since the carbon to graphite reaction produces very little heat, this reaction may overrun the steady state conditions and produce a liquid iron that is so depleted in carbon that it becomes hypo-eutectic. See the description of hyper/hypo-eutectic mode below.

The eutectic mode of freezing is preferred for smaller castings. The higher carbon and silicon content promotes graphitization and prevents chill. As stated before, this mode of freezing extends from about a 4.33 C.E. up to a 4.55 or even 4.60 C.E. The uncertainty of lab results plus other possible variations such as effective magnesium may vary the upper limit. As we know, foundry labs vary in their chemistry calibrations and the effect of different levels of Mg/Ca has not been evaluated, so the upper end may vary accordingly. But what is most notable is that it is a single arrest. MeltLab is very sensitive to different arrests, and will catch a weak austenite arrest where other instruments will not. (The weak austenite arrest requires the second derivative to detect.) Eutectic irons are slow to develop wall strength, and so are subject to suck-in in heavier sections. Their gates are also slow to close (no dendrites) and so solid risers may occasionally be a problem. So if you have solid risers and eutectic mode freezing you might want to try smaller gates.

The final mode of freezing could also be called a disaster. It is when you have a graphitic liquidus followed by an austenitic liquidus. Professor Heine published a paper in the early 70's on thermal analysis of Ductile Iron, where he clearly shows this happening in what he called hyper-eutectic (based on chemistry) iron. The graphitic liquidus removes enough carbon from the liquid to drop the liquid to a hypo-eutectic state. So even though you have added more carbon to fight shrinkage, you are faced with even greater shrinkage than before.

Early verses Late Graphite

Gate freezing and wall strength development are key factors in obtaining solid castings. Ductile castings are actually steel castings containing graphite. The matrix of the casting is a steel with a 10% shrinkage rule, and the graphite component consists of carbon that went from no volume in the liquid to occupying 9 to 11% of the volume. To make this miracle help us, we need to keep the expansion due to graphite inside the casting. If the gates are slow to freeze off, then this expansion will just push iron through the gating and into the risers. If the walls are slow to develop strength, then it could cause the casting to swell. The cure for this of course, is to try to form more graphite during the later stages of freezing. Inoculant suppliers have come to the rescue with various inoculants that are better at late stage graphitization. Both MeltLab and ATAS look at the amount of graphite produced during the eutectic stage of freezing, but we use different methods. The first stage of freezing is defined as the period between TEU and TER or between the eutectic undercooling arrest and the eutectic recalescence point. The second stage is defined as the period between the TER and the point where the eutectic reaction dies. We use the end of eutectic growth point on the curve as defined by the 5th derivative. Since ATAS can't do higher level derivatives, we are not sure how they determine the end of their second period.

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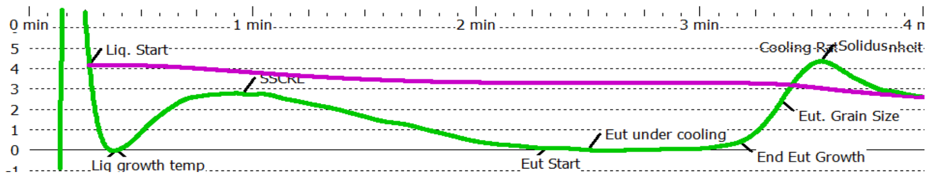


Cooling rate curve (green) with the zero curve (magenta) for a ductile iron showing various points determined by MeltLab

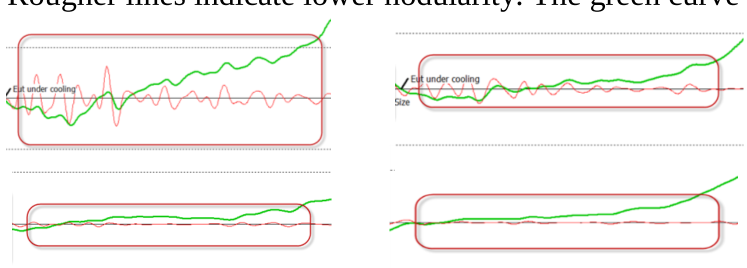
The final difference is that we then measure the energy released during the two segments, and not just the time. The energy is the area between the rate of cooling curve and the base line or zero curve. We integrate that area for the two sections and divide the total energy into the energy of the second section. The above example has 83% late graphite growth and is from a hypoeutectic iron.

Graphitization

Another measure is how graphitic the iron is or how much graphite did we squeeze from the matrix. Pearlitic irons are pearlitic because they retain carbon and form less graphite. Assuming a 3.8% carbon, 20% of the carbon would have to remain in solution to make a fully pearlitic iron. So the completeness of the graphitization process is useful to know. ATAS uses a G Factor to measure this. To be different, MeltLab uses a ferrite calculation instead. Manganese, chrome and other carbide forming elements form larger holes (interstitial spaces) between the iron atoms where carbon can hide. These effects lead to lower energy production at the end of the graphitization. Likewise highly ferritic castings are added by short diffusion paths between nodules so higher nodule counts help ferritize the iron. MeltLab looks at both effects to predict nodule count and ferritization as two separate and useable pieces of information in making good castings.

Nodularity

ATAS doesn't do nodularity so we can't describe their methods. Instead we will say that we have found that vermicular and poor forms of graphite grow in spurts, just as flake graphite does. Spheroidal graphite grows by diffusion and is much steadier in its energy production. We look at the smoothness of the eutectic reaction by measuring the individual measurements of the 5th derivative and taking a standard deviation of points that should be a straight line if we had smooth, steady growth of diffusion fed nodule growth. Rougher lines indicate lower nodularity. The green curve is the rate of cooling, the



80%, 85%, 90% and 95% nodularity examples

red curve is the 5th derivative. The Scale lines for green is 1 degree F per second. The scale line for the 5th derivative is 1/1,000 degree F per (second)^5.

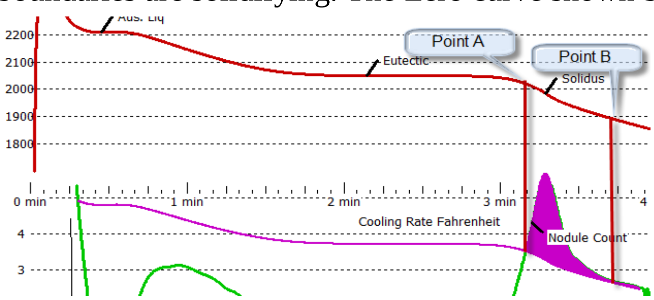
Shrinkage

Shrinkage is a tough problem for many foundries. There is the usual finger pointing between foundrymen blaming generally in the order of: 1.) the gating and risering, 2.) the pour temperature and metal chemistry and inoculation, and finally 3.) the sand. Gating and risering has the easiest job. They can always say: nothing has changed since it ran well last time. Sand and metal have a harder job explaining why shrink can come and go. While TA may not have all the answers, it can help enormously to understand the problem.

Thermal analysis cups have a fixed mass and a fixed cooling rate. It may not be the same as the casting we are having problems with. But the characteristics of the cup may indicate the characteristics of the casting. From the discussion above, we have indications of the freezing mode, the amount of late graphite and the percent of ferrite/pearlite due to chemistry. The overall effect creates a situation that can increase or decrease the probability of shrinkage. Other causes are the casting design, and the gating and risering. If you can design a gating and risering system that will at times give a solid casting, then thermal analysis will allow you to set a benchmark for that casting, and determine how close you are to repeatedly making the best iron for that casting. If you make bad castings then you can compare the parameters that worked before with the parameters that didn't work and then determine if it was chemistry or inoculation that was off. Tighten the controls of the errant parameter and stop making bad castings.

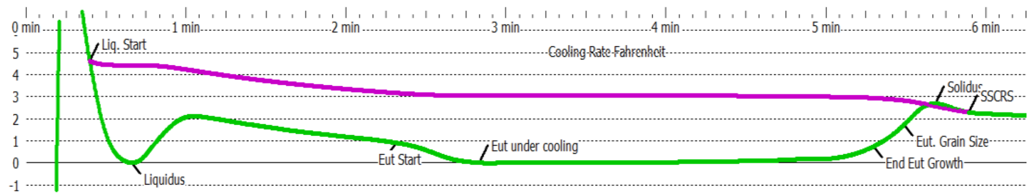
Here is an additional parameter that can help with small to moderate size castings: a shrinkage factor. ATAS looks at the height of the solidus arrest on the rate of cooling curve as an indicator of shrinkage. More height is better. In the usual answer to the question "Why?" from NovaCast gives us the famous line "we don't know". As a metallurgist, I have always disliked that answer. Saying that correlation studies show that the number is significant without a background understanding is like saying there are more drunk Irishmen on the streets on Fridays and Saturdays than on Sundays. Digging a little deeper, you would find that Irishmen have plenty of causes to drink (the British for one), and that they usually get paid on Friday, and are in Church on Sundays thereby explaining that having money correlates equally as well and is a more likely cause than the day of the week.

So what of this curious area of the thermal curve? First, it is clearly endothermic or heat absorbing. Second, it is not shrink, even though shrink is also endothermic. And finally, it occurs just as the grain boundaries are solidifying. The Zero curve shown below in magenta slices through it giving an area proportional to the energy absorbed by the strange feature. Ratioed against the rest of the curve, the area reaches a maximum of 10 to 12 percent of the total energy of solidification. The answer we came up with was that this is stress in the grain boundary. As the area decreases the stress is being relieved either though shrinkage or suck-in.



Square Electronite non-tellurium cup cooling curve

If a much slower cooling rate is used, the same iron will produce less stress as the graphite has more time to form as seen to the right.



Round, coated ElectroNite non-tellurium cup with fiber cloth covering

Using the faster cooling rate of the square cup, we can see the overall effect of wall strength, graphite growth and total graphite formation. We cannot see the effect of early vs. late graphite formation, because the cup is not a gated or risered casting. Stress can only build up if the casting walls are strong and the shrinkage forces do not exceed the capability of the grain boundaries to absorb stress. There is one other idea that has not been previously mentioned, and that would be if there are shrinkage nucleation sites in the casting. I believe this is the first time such an idea has been expressed. But consider that forming an interior surface takes a certain amount of energy. If that energy is not exceeded, no shrinkage occurs. A gas bubble - or perhaps something else - could nucleate the interior surface. I will leave that for others to look at.

Summing up ductile iron controls

We have modes of solidification: hypo-eutectic, eutectic, hypo-eutectic, and the combination of hyper/hypo-eutectic. Hypo-eutectic is the preferred mode for thick section iron, and eutectic is the preferred mode for thinner section castings. The eutectic mode extends from 4.33 C.E. up to between 4.55 and 4.60 C.E. with hyper eutectic modes above that. MeltLab presents this as the Freezing Mode.

Later graphite is preferred over early graphite to give the casting gates more time to solidify. As graphite grows, it replaces the natural shrinkage of the steel matrix. If this growth is retained in the casting by the gates freezing off before much graphite growth has occurred, we can hope for solid, near net shape castings. If too much graphite growth occurs before the gates freeze off, we will have solid risers, and holy castings. MeltLab presents this as the percent late graphite.

The degree of graphitization is the degree that the carbon converts into graphite. Small amounts of carbon always remain in the iron matrix, even in fully ferritic castings. This carbon is converted to graphite during heat treatment and increases the graphite in ferritic castings from an average of 10% volume to 11-12% of volume, and changes the elongation values from 8% up to 12% and higher. Less graphitization means shrinkage is more likely. Pearlitic irons are therefore more prone to shrinkage than ferrite irons if all other things are equal. MeltLab presents this as the percent Ferrite.

The Shrinkage propensity of the iron is a combination of the wall strength, the graphite growth, and any shrinkage nucleating effects in the iron. We often see either fine scattered shrinkage or large agglomerations of shrinkage. If the shrinkage is nucleated early on, we would then expect fewer but larger voids. If the shrinkage is delayed until the very last of solidification, we would see fine scattered porosity. MeltLab presents this as the Shrinkage factor.

While not as polished as ATAS, MeltLab offers solid values based on the science of metallurgy, not just correlation studies, and for less than half the retail price. What may we do for you?