Iron Recalesence

By Yohan Tremblay and David Sparkman
December 2015

Executive Summary:
This complex arrest in iron tells us about the physical properties our castings will have. It is sensitive to the chemistry and the inoculation of the iron, and can determine if the iron has been properly prepared for pouring. When an iron solidifies, the eutectic reaction shows recalesence in all but the deadest of white irons. This applies to grey, ductile, and compacted graphite irons. This, together with [1]the thermal analysis of carbon equalivant, graphite formation, shrinkage, and pearlite measurements give a complete picture of the iron preparation process. MeltLab measures recalesence and helps operators to adjust iron for consistent castings.

Definition
Recalesence is a term from French that means reheating. In Metallurgy it is used to refer to the difference between the undercooling of an arrest and the maximum temperature of an arrest. It is occasionally seen in the Liquidus arrest, but is most common in the Eutectic arrest in an untreated thermal analysis cup. Below is a typical curve for a moderate size casting with a C.E. of 4.43 of nodular iron using a plain non-tellurium cup. The TEU or eutectic undercooling occurs at 2096.8 and the TEG or maximum temperature of eutectic growth occurs at 2107.9 The difference (2107.9 - 2096.8 = 11.2) is the recalesence.

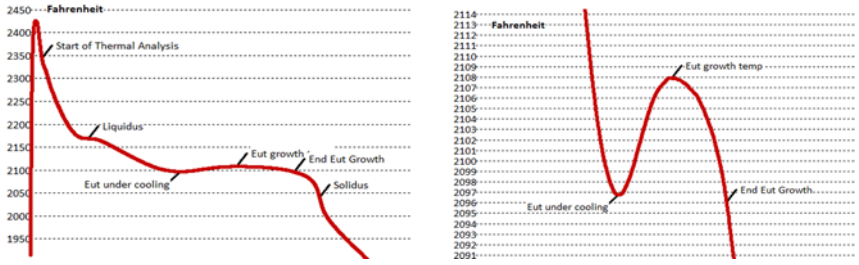

Fig 1 Typical Eutectic arrest in iron and zoomed in

Activation Energy: https://en.wikipedia.org/wiki/Activation_energy
From Wikipedia: *"Activation energy may also be defined as the minimum energy required to start a chemical reaction."* The undercooling of the eutectic provides this activation energy to get the eutectic started. Some authors have suggested that there is a first and second eutectic. I believe this is wrong, because if it were so, then no activation energy would be needed after the first eutectic started. The arrest these other authors are seeing is just an austenitic precipitation that further raises the carbon content to full eutectic concentration. Activation energy is still required. Thermal analysis is still uncovering secrets.

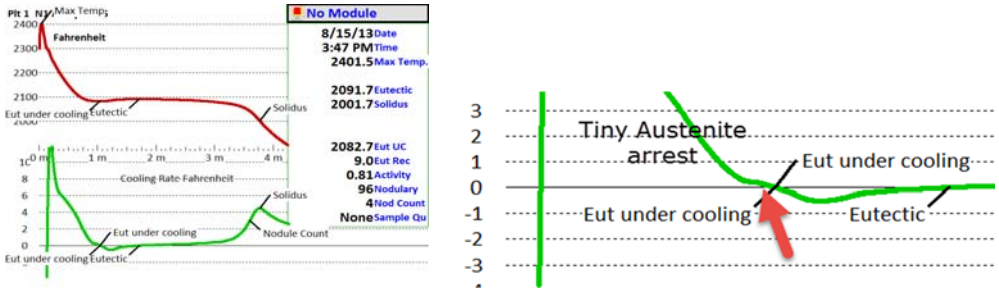

Fig 2. Austenite arrest in eutectic iron

[1] See our other papers on these MeltLab thermal analysis methods

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The eutectic energy release

Graphite can grow in both the austenite and in the eutectic material[2]. Austenite grows as dendrites often with slow growing graphite nodules embedded in their arms. Austenite can only contain 2 % carbon at the eutectic temperature (less at room temperature), so the excess carbon is pushed into the remaining liquid raising its carbon content until saturation is reached. The eutectic material provides the bulk of the energy of solidification in all irons and contains considerably more graphite than the austenite. While austenite seldom shows recalesence, the formation/nucleation of graphite in the eutectic is difficult and does require activation energy. The better the nucleation in the iron, the easier it becomes to start the massive energy release of the eutectic.

Consider the reaction from two perspectives: the forces promoting graphite and the forces inhibiting graphite. The forces that promote graphite formation are the carbon and silicon gradients in the metal, and the seed crystals formed by the inoculation of the metal. The magnesium inhibits the formation of graphite and so more undercooling of the eutectic is required to trigger the reaction.

Carbon is generally evenly distributed though out the eutectic so higher carbon contents assert pressure on the iron to form graphite. Irons that are hypo-eutectic will remove iron from the melt in the form of austenite until the remaining liquid is of at least eutectic or higher composition. Irons that are in the eutectic zone of 4.3 to 4.6 C.E.[3] can begin forming eutectic graphite with little or no further austenite formation. Still some small amounts of austenite are sometimes found.

Hyper-eutectic Iron – not for most foundries

Hyper-eutectic iron is generally only used for small thin castings that need excellent flowability. The tradeoff is that this iron is very prone to shrink. With very thin castings this is generally not a problem. Above about 4.6 C.E. graphite can begin to form in the liquid. This produces a weak graphitic liquidus which will quickly withdraw carbon from the liquid pushing the remaining liquid to below eutectic composition. The main effect of a graphitic liquidus is solid risers and massive shrink in all but the thinnest of castings. This is a problem in foundries that run too close to the edge. A small jump in carbon or silicon puts the iron above 4.6 C.E. and disaster strikes.

Hypoeutectic Iron – for large castings

Heavy section iron is usually cast as hypoeutectic (below the eutectic) iron. This produces abundant dendrites of austenite to quickly form wall strength and prevent suck-in. Gates have to be larger to prevent the dendrites from closing them off, and heavy section risers are needed to feed the casting. Controlling the C.E. controls both feeding and wall thickness but lower C.E.s require more feeding. Higher C.E.s may not develop enough the wall strength quickly enough to resist suck-in. The challenge is getting the right balance of gate size and C.E. and controlling the C.E. to the same level each time. Changes in C.E. levels often require enlarging or shrinking the gating.

Eutectic Iron – for medium size castings

Medium size castings can and often do use eutectic (single freezing arrest) iron to make mostly solid castings. By keeping the C.E. toward the high end of the eutectic range (4.5-4.55 C.E.) more graphite is produced and in theory less shrinkage is developed. As has been shown in other papers from MeltLab, shrinkage depends on a multitude of factors. Choosing a C.E. level and sticking to it and adjusting the gating to close off before the formation of graphite are just the first steps in avoiding shrinkage. There are also issues of inoculation control and iron cleanliness that need control to avoid shrinkage.

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[2] *Examination of Nodular Graphite Formation and Austenite Solidification in Ductile Iron,* J. Qing et. al. AFS Proceedings 2015 paper 15-072

[3] Eutectic has two meanings – the lowest melting point and a single arrest. Iron exhibits a “singe arrest” between approximately 4.3 and 4.6 C.E. With eutectic the gates stay open longer and wall strength is slower to develop.

As we've seen, it's important for foundries to control their solidification mode (or freezing mode?). Problem occurs often when you jumped to another freezing mode. That's why carbon equivalent measure is important and best way is thermal analysis. Using the old carbon equivalent calculation of (C+1/3Si+1/3P) is not accurate enough to know you're freezing mode.

Promoting Graphite – the pushing factor

Many think the remaining silicon is also evenly distributed in the eutectic. There is reason to believe that this is not the case. Scientific American published an article many years ago on super molecules that suggests that some molecules do not quickly disperse throughout the liquid. Silicon seems to be one of these. It is well known that simple 75% FeSi promotes nucleation in gray iron for up to 15 minutes in a ladle. Why would this be time limited unless the silicon takes 15 minutes to evenly disperse? So there are probably areas of high silicon which would help promote graphite nucleation. Another theory holds that the seed crystals formed from the ferro-silicon migrate to the slag or walls of the container and so are removed from the metal.

The important thing is that certain crystalline shapes closely match the lattice spacing of graphite. That is that the distance between atoms of the seed crystal is very close to the distance in graphite between the carbon atoms. This provides the initial structure for graphite to permanently form, and not redissolve. The binding forces of the seed crystal being either an oxide or sulfide or combination, are much stronger and have melting points far above the temperature of the liquid metal. The graphite of course has a melting/dissolving point that is almost the same as the molten metal temperature. By super-cooling, the graphite gains some stability and persistence. By using higher super-heat temperature, you'll produce more oxide and increase your récalescence.

Squeezing out the carbon

The carbon atom exists in molten iron by "hiding" between the larger iron atoms. Iron first forms into a crystalline form called Face-Centered Cubic or FCC. This is the familiar material called Austenite. There are holes in this structure between these large atoms where smaller atoms may fit.

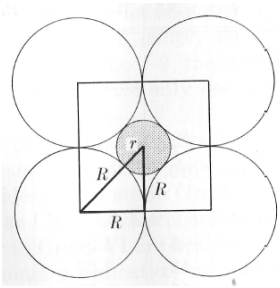

Fig 3. Four iron atoms of FCC Austenite having radius R and one carbon atom squeezed in having radius r.

Using the Pythagorean Theorem with the Figure 3, the long diagonal (corner to corner) is:

$(R+2r+R)^2 = (2R)^2+(2R)^2$

$(2R+2r)^2 = 2 * (2R)^2$

$2R+2r = Sqrt(2) * 2R$

$2r = (Sqrt(2) * 2R) – 2R$

$r = (Sqrt(2) * R) – R$

$r/R = (1.414 * 1) – 1$

$r/R = 0.414$ Likewise $2r/2R = 0.414$ or the smaller diameter is 0.414 * the larger diameter.

The diameter of the iron atom changes with temperature starting from 320 pm (picometers) at the liquid/solid temperature and dropping to 286.6 pm at room temperature. This gives a hole diameter of 72 pm at the start of solidification. That is just enough for carbon at 69 pm to squeeze in. Nitrogen also fits in at 71 pm.

As the metal cools, the solubility of carbon in austenite decreases pushing more carbon into the eutectic and also causing the graphite forming inside the austenite to grow. This would suggest that higher Carbon irons would need less undercooling to get the eutectic graphite reaction started.

Nucleating Graphite – the pulling factor

Graphite and most other metallic crystals have a problem in nucleating. As soon as 2 or more atoms unite, they are often broken apart by thermal energy. What is needed is a substrate that is stable i.e. has formed at much higher temperatures and does not redissolve at the eutectic temperature. In addition, the substrate must have a structure that is close to the size and spacing of the graphite crystal. To be stable, these substrates are ionic in nature – built from different inclusions like oxides, sulphides, nitrides and silicates with various metals. The better inoculates promote the formation of such substrates.[4]

One such component is magnesium as is used in compacted graphite and ductile iron. Although many successful substrates contain magnesium, a problem is created in that magnesium changes the surface tension of iron and suppresses the formation of flake graphite. This forces a delay so that either late forming vermicular graphite or, at higher concentrations, late forming spheroidal graphite is made.

Understanding what Recalesence is telling us

There are then several factors in the eutectic recalesence that can be measured:

- The temperature range TEG – TEU required to start nucleation
- The speed of recalesence which depends on the number of nuclei
- The heat production during eutectic recalesence which depends on the amount of eutectic material vs. dendritic material. This can be further divided into two parts: early and late graphite formation.
- The speed of temperature loss at the end of recalesence which also depends on both the number of nuclei and on the amount of residual carbon which will later form pearlite/martensite.

Temperature Range

The temperature range of recalesence is then a factor of both chemistry and nucleation. As such, it is a quality control point. Deviation from its standard value can tell you that the iron chemistry is out of bounds and/or the nucleation is wrong (generally low).

Speed of Recalesence

The speed of recalesence is how quickly the metal reheats to the eutectic growth temperature. This is entirely due to the distance between nucleation sites (length of the average diffusion path). This is another way of looking at the number of nucleation sites, or in ductile iron, the nodule count. Higher numbers of nucleation sites will decrease the distance carbon travels to such a site, and increase the speed of energy release. This shortens the time to achieve the maximum eutectic temperature (TEG). One problem in these measurements is that under filling the cup causes the thermal couple to be away from the sample's center of heat and due to chilling, the recalesence may be understated. One sure proof of a good sample is a flat ceiling in the eutectic. The temperature has reached its maximum and cannot go higher without remelting.

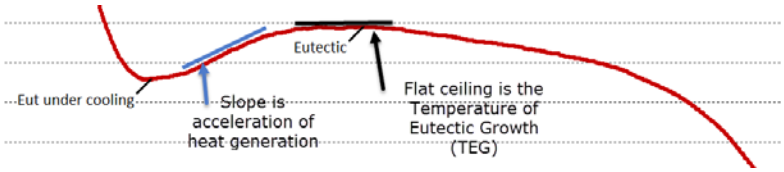

Fig 4 Acceleration of heat generation and TEG Ceiling

[4] Nucleation Mechanisms in Ductile Iron, T. Skaland, Elkem.
Cees Vandevelde http://www.ceesvandevelde.eu/dltweedis.htm
Solidification of Ductile Iron Revisited (AFS Transactions 11-064), S.Viswanathan

The cooling rate graph is just the first derivative from calculus flipped over. Therefore the lowest point on this green curve is the steepest slope of the temperature curve going into the eutectic and the rate of heating at this point is simply -1 x the Rate of Cooling. Likewise the flat ceiling from the previous graph shows up here as a flat spot at zero showing that the temperature is stable for a number of seconds.

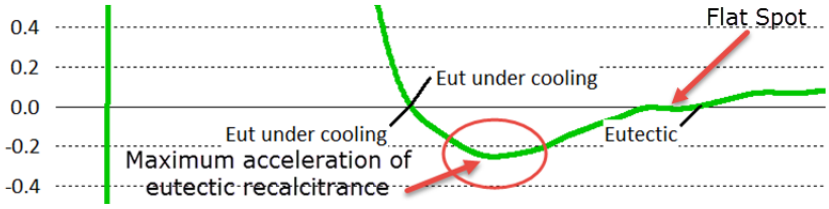

Fig 5 Cooling rate shows minimum cooling (maximum heating) during acceleration of heat generation

The heat production during the eutectic growth area is limited by the chemistry of the iron. The temperature reaches a ceiling as dictated by chemistry (TEG). If the temperature went higher than this ceiling, it would remelt and become liquid again. So the maximum temperature bumps along under this ceiling. As higher temperature material solidifies out, this ceiling slowly moves downward. Some early authors found a crude relationship with nodularity and this slope. This may just be happenstance. Work with other alloys such as high purity aluminum (99.99%) which has no nodularity component shows a similar fall off as the small amount of impurities becomes more concentrated in the remaining liquid.

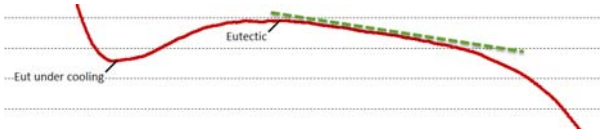

Fig 6 Eutectic ceiling drops as higher temperature components solidify out of liquid

Finally, the speed that the eutectic recalesence ends tells us how the energy has gone out of the reaction. Since the rate of depletion of carbon in the liquid controls how fast the austenite can form from the eutectic liquid, the number of nucleation sites again control how the eutectic arrest ends. With higher nucleation sites and therefore shorter average diffusion path lengths, the reaction goes to completion quicker and the reaction ends more abruptly. This can be very important to controlling micro-porosity form of shrink. The more graphite that forms before solidus, the more volume is added to the casting.

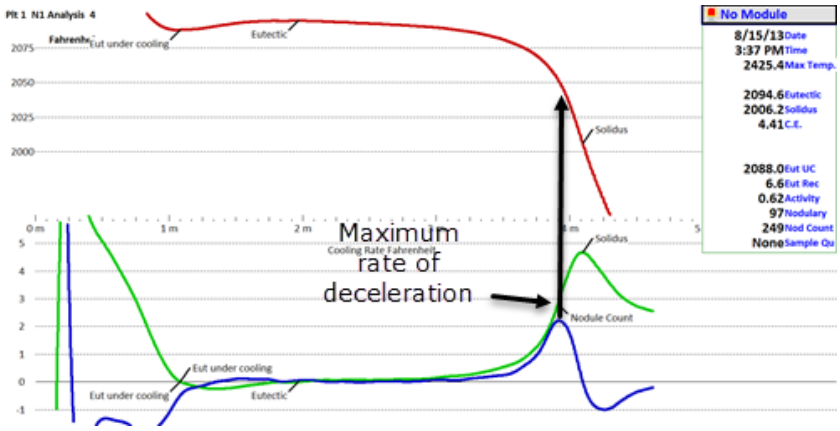

Fig 7 The eutectic reaction comes to completion showing degree of inoculation

As has been noted in other papers, this point of the maximum deceleration of heat is also commonly the point where shrinkage arrests can occur and interfere with reading this value. The good part is that higher levels of inoculation prevent or severely repress micro-porosity shrinkage.[5]

Conclusion

Recalesence is a function of the chemistry, inoculation and nucleation of an iron. Different chemistries and inoculants will control the degree of recalesence. Variation is introduced by the raw materials, variation in supplier provided inoculants, and in methods and the skill of the people processing the iron.

Higher carbon content and good inoculation will promote the extraction of carbon from the liquid to more quickly release the heat of solidification by shortening the distance carbon has to move to a graphite site. The number of nucleation sites may be indicated both by the speed of recalesence to the TEG point and by the deceleration of heat generation at the end of the eutectic. Since some nucleation sites probably form during the latter part of the eutectic, the second method may prove more reliable.

Application

Process Control requires measurement of critical factors. Assuming all is well because we always did it that way is a risk that cannot be taken in a modern foundry. While it is always possible to test after the fact and prevent serious problems from reaching your customer, true process control starts early and prevents and corrects problems before things get out of control. There is no easier, inexpensive, and reliable way of checking the preparation of the iron for the mold than a simple thermal analysis cup. And, with good corrective actions, your product will be far more consistent day after day from operator to operator.

MeltLab Systems

While there are many different instruments on the market, the modern ones are following the lead of MeltLab. This includes ElectroNite and ATAS as well as various companies in Europe and India. With MeltLab you get state of the art metallurgical information from those who know metallurgy and can answer your questions.

Foundry Solutions & Metallurgical Services Inc. (SF)

When it comes to implanting the best practices on the foundry floor, SF is the partner par excellence. We know what to measure and control on the foundry processes, such as metallurgy and molding parameters, in order to provide process control for more consistent castings. Thermal analysis is the perfect tool to measure and control metal quality and prevents related scrap.

[5] For more information on how other forms of shrinkage (macro porosity, gas porosity, and suck-in) see our research on Shrink. Request at info@meltlab.com