Ductile Nodularity by thermal analysis

By David Sparkman – MeltLab Systems 2008

Abstract: This paper shows how MeltLab measures the smoothness of the curve to determine the degree of nodularity of a final ductile iron sample. Taking the casual observance of Dr. Lampic, we have turned up a surprisingly reliable way to measure the growth shape of graphite by the bursts of energy produced by the growth on vermicular graphite. This method is ideally suited to MeltLab's strong points of precision, noise suppression, and derivative calculation.

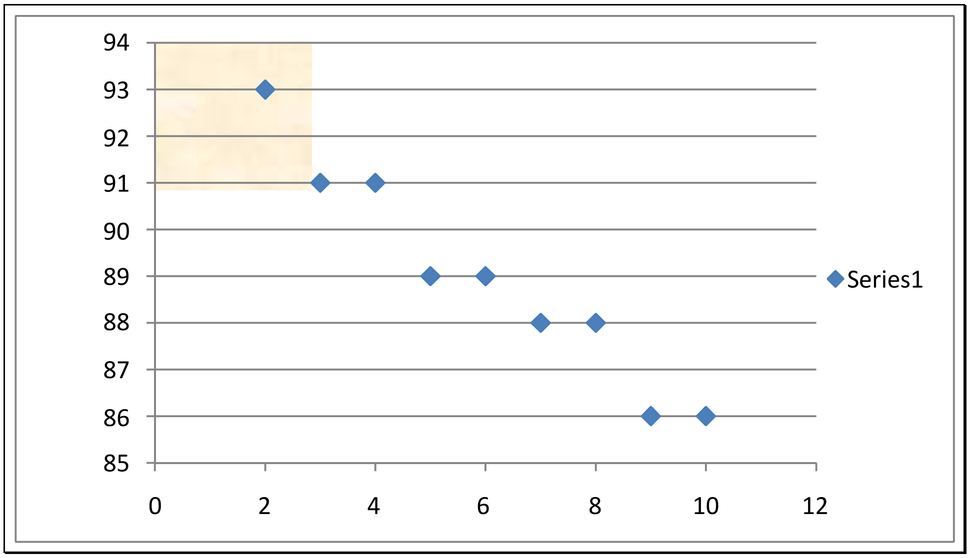
Introduction

Nodularity shows itself by the smoothness of the temperature curve during graphite formation. On the other hand, vermicular graphite grows in spurts and roughens the curve. Finally, if the inoculation/treatment fails, you have massive roughness in the curve due to D and E-Flake formation. This was first commented upon by Herr Doktor Lampic of Fritz-Winter of Germany in some oral presentations here in the states. I came across some of his handouts and took it from there.

A tool to measure

Looking directly at the temperature curve, you have to have a very good eye to notice the bumps. But by zooming in you can notice the differences between curves. Putting a number on it was a challenge. Looking at the first derivative, there were large swings over the entire curve as different thermal events happened. But the area where graphite growth happened during the eutectic did show the roughness. Because of other events such as gas happening, I choose the second half of the eutectic to concentrate on. This area gets hit by shrinkage, and carbides (carbides are linked to shrinkage because they limit the amount of graphite precipitated). Moving down to the 4^{th} derivative, this roughness appeared as an oscillation along the zero value. The oscillations were large with poor nodularity and small with good nodularity. If shrink or carbides occurred, the oscillations went wild.

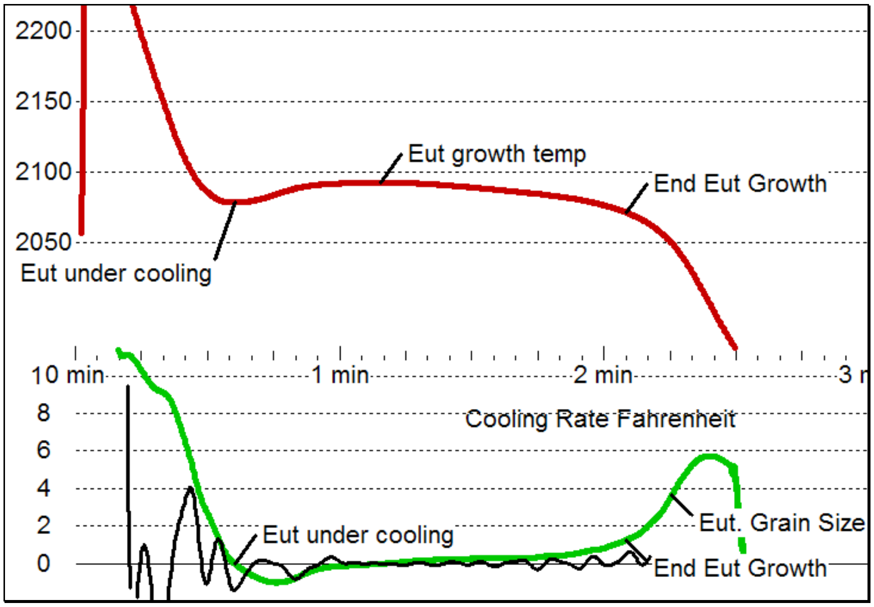
To get a measure of the oscillations, I simply took each value from the TER point (temperature of eutectic recalesence) and the EGE (end of graphite energy) point and ran it though a standard deviation equation ($\sigma = \sqrt{x^2/n-1}$) n-1 being used for larger populations. Running the results though a natural log function then produced a more or less linear relationship. Somewhere below 80% nodularity, carbides destroy the relationship, but since we are trying to measure from say 75% to 100%, the results were satisfactory and useable. Anything below that was certainly not good iron.



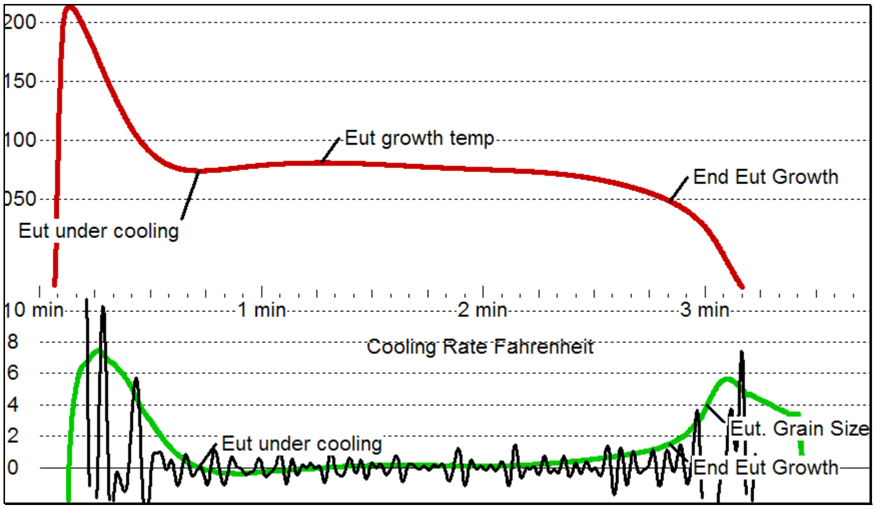
Based on my experiences and the research of many others, my best explanation of the nodularity formation in the following sample are as follows:

First, the magnesium content of the liquid iron goes down during the formation of graphite. Basically it is consumed forming sulphides and oxides and other complex molecules that serve as the seed for the nodules. Therefore, vermicular graphite and other less desirable forms of graphite/carbide if present will form toward the end of the eutectic. I have determined a point where the energy production sharply falls off. This is labeled as the end of Eutectic Growth. For those purists the Eutectic growth temperatures shown below are actually the graphitic eutectics. Proof is provided by zooming in on the actual EGT and seeing that the curve is flat for 10 to 15 seconds. The temperature is physically bumping against a ceiling temperature proving it to be the true graphitic eutectic.

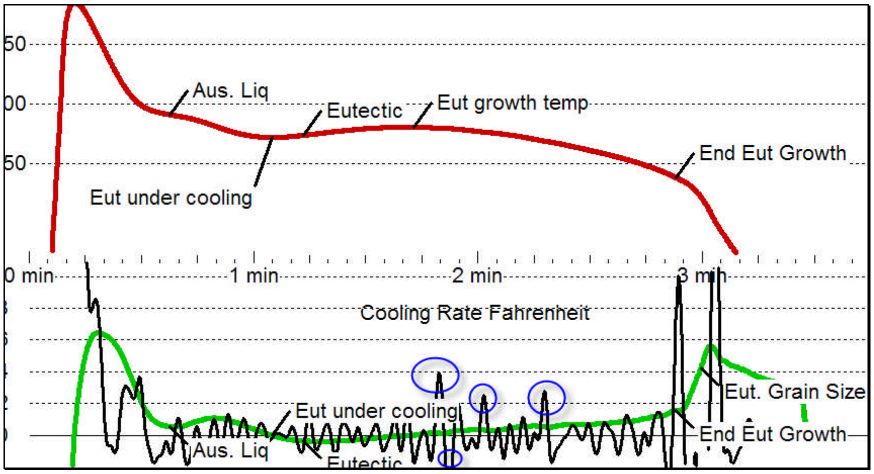
As a previous Quality Control and Quality Assurance manager for Dana Corp, I have an aversion to rating anything as 100% nodularity. My highest numbers are capped at 99% nodularity so that no customer finding one small piece of vermicular graphite can challenge the 100% rating. Yes some customers are that picky. The following samples were from production ferritic ductile iron and measured using a small round sample cup from MINCO with the tellurium pill removed. Such cups can also be ordered in bulk without tellurium. Square and larger round cups can also be used, but the cooling rates are a little different, and the equations must be tuned to those rates. It is also critical that the cups not be under filled. Serious under filling will cause the area around the thermal couple to cool much faster and give false readings.



This sample was 99% nodularity with very low pearlite content (65-45-12). The black line is the 4th derivative.



This sample was captured with a little higher rate of sampling but shows the start of nodularity deterioration toward the end of the eutectic. This was rated as 93% nodularity.



This sample shows considerably more roughness during the eutectic. This was rated as 85% nodularity and has a lower ferrite rating as well as an austenite liquidus. The blue circles show points of roughness caused by changes in growth rates of the graphite and austenite.

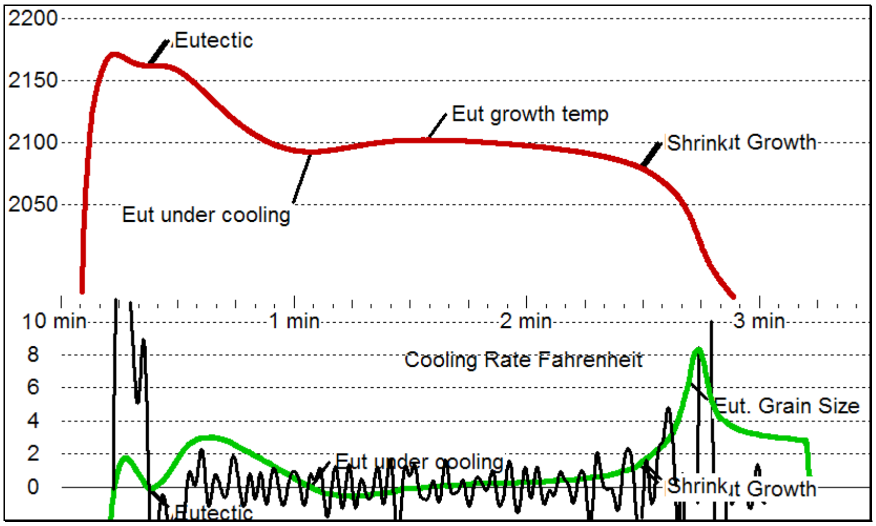
Needless to say, this is a difficult test that as of this date, 2008, most thermal analysis systems cannot measure. MeltLab, by using a constant voltage power supply, a very good 16 bit analog to digital convertor using two wire shielded thermal couples, and some advanced smoothing techniques is the only system, commercial or research that is able to pull out a good, solid 4th derivative.

Limitations and Methods

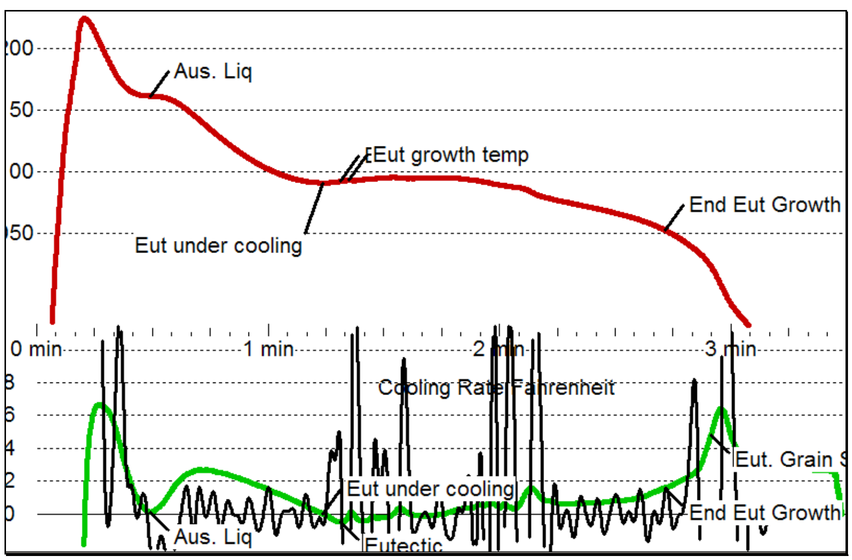
First, this method will only work on final ductile iron. The sample must be properly treated, and inoculated to reflect the condition of the iron forming the casting. Some ductile irons are gassy and produce large gas bubbles in the eutectic that interfere with the nodularity readings. I have not seen this often enough to know exactly why this happens, but it needs to be checked to see if it is a potential problem with the MeltLab, and, possibility a problem with your castings as well.

And finally, some cups are not well made and can have thermal couples that partially fail. This is seen as a rapid temperature drop of 10 to 20 degrees caused by the molten metal breaking though the ceramic or glass tube protecting the thermal couple. All you can do is get another box of cups and send the bad ones back to the manufacturer. Currently, manufactures don't pay this defect much attention. It is caused by thinner quartz tube walls (read cheaper), bent quartz tubes (machine screwing up, or thermal couples welded by hand inside the tube), and low density ceramic tubes (tube supplier problem).

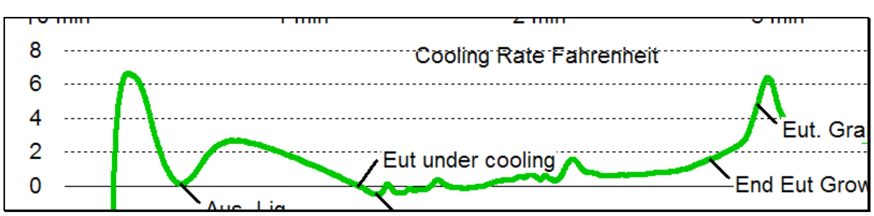
A little extra
This same method when applied to gray iron gives some surprising results. The 4th derivative is giving changes in the rate of cooling due to the growth of different types of graphite. In this case it is a difference between normal A flake and lower quality flake types. There is more work to be done in this area but it looks very promising as a check on inoculation.



Well inoculated Gray Iron



Opps – a problem with the inoculation addition?



The same bad curve as above just showing the bumps in the cooling rate.