Hot Topics in Thermal Analysis

Information on Thermal Analysis for Foundries

Dual Cup Analysis for Iron – October 2010

The dual cup analysis system was pioneered by MeltLab in the early 1990's as a way of getting chemistry, chill, and inoculation information in a single step. The method was to simply pour both a tellurium cup and a plain cup from the same spoon of iron in quick succession. Besides the extensive analysis of both kinds of cup (chemistry and microstructure) we were also able to compare the "distance" separating the grey and white eutectics (stable and metastable). The greater the distance between the two in terms of temperature, the softer the iron was.

We published a paper with AFS on comparing chill wedges to the separation between curves back in 1996. There is a lot of human variation that goes into chill wedge readings that can be removed by DualCup.

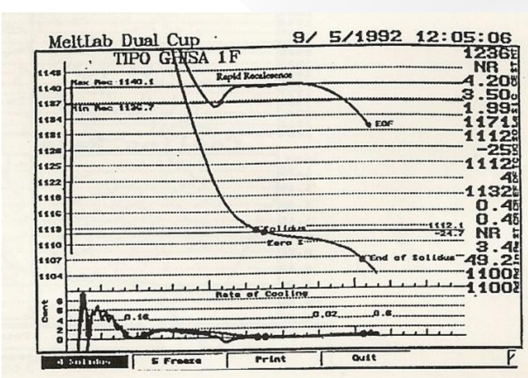
The concept of chill measurement by thermal analysis is documented in my paper "Chill measurement by Thermal Analysis", AFS Transactions, 1996, page 969. The separation between the graphitic eutectic and the white/metastable eutectic is both a measure of the grade of iron, and the chill potential of the iron. A G25 iron will have a large separation, while a G45 iron will have a much smaller separation. But rather than just specifying the grade, we can draw a finer distinction between the different heats to the point of actually predicting the chill by using the metastable eutectic and the eutectic undercooling temperature. Since the degree of undercooling is directly affected by the inoculation, this factors in both the overall chemistry and the inoculation into the chill calculation.

$$\text{Calculated Chill} = (k_1 * \text{C.E.}) + (k_2 * (\text{TEU} - \text{TCE}) + k_3$$

or

$$\text{Calculated Chill} = (k_4 * \text{Liquidus}) + (k_5 * (\text{TEU} - \text{TCE}) + k_6$$

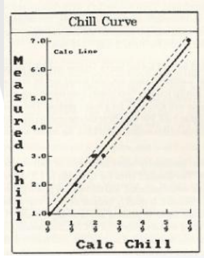
C.E. = Carbon Equilivant derived from the Liquidus temperature
TEU = Temperature of Eutectic under cooling
TCE = Temperature of Carbidic Eutectic (metastable or white eutectic)



The example to the left was from an Italian foundry with 25˚ C separation between curves. The screen shot is from the previous version of MeltLab. The upper graphitic curve shows a beautiful cap or ceiling eutectic arrest showing that the 1140.1˚ C is the true eutectic temperature and was not affected by the rate of cooling. The eutectic undercooling of 3.4˚ C indicates the degree of inoculation.

Though I am no expert in all the ins and outs of chill wedges, here are a few things I have learned:

- Chill wedges come in different sizes. The correct size for you depends on the wall thickness you are pouring. I have seen wedges from 1 inch high to 8 inches high.
- The wedge mold must be free of dirt and loose sand that would blunt the edge of the wedge. The heat of the iron will affect the chill, so try to pour the wedge at a constant temperature.
- If also pouring thermal analysis cups, pour the wedge first, not last, as it is more affected than the cups by temperature.
- The best technique I ever saw was in an AFS inoculation course. The technician took a second chill mold and struck off the top of the poured mold to wipe off any excess iron and the miscues. Then, promptly at 60 seconds, he tossed the entire mold into a bucket of water. (You might have to change that time with 8 inch wedges.)
- The wedge needs to be broken at the same distance from the pour basin each time. Closer to the pour basin will show less chill, further away will show more. Most molds have a small break line embedded into the core.
- And finally, there is some disagreement on how to measure the chill. Some measure from the point, some measure the width of the wedge at the first point of no chill. I hold with the width measurement because it is less affected by dirt in the point of the mold.



Chill Results for Medium Sections

Liquidus	Delta °C	Chill mm	Calc Chill	Error
1204	26.7	20	20.311	0.311
1200	27.2	18	14.572	−3.428
1202	25.7	20	20.244	0.244
1199	27.8	11	12.071	1.071
1199	29.2	9	8.932	−0.068
1198	29.3	7	7.553	0.553
1200	26.7	14	15.693	1.693
1199	28.0	12	11.623	−0.377

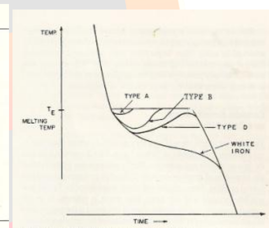


Fig. 2. Undercooling effects on structure formed.

Images from the paper *Chill measurement by Thermal Analysis*, AFS Transactions, 1996, page 969 by David Sparkman and Charles Bhaskaran available for a fee at http://www.afslibrary.com/.

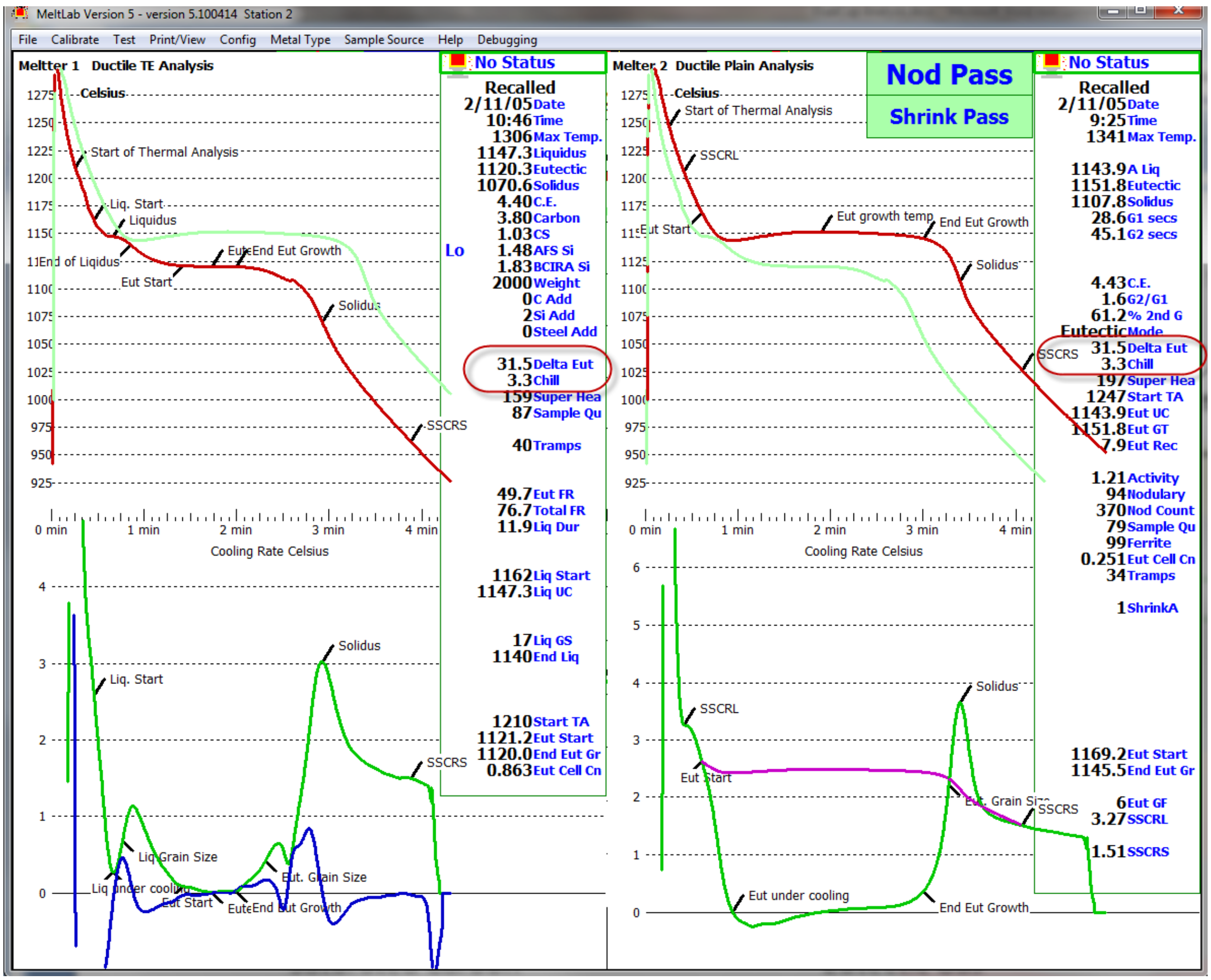
If you want to use the dual cup method to calculate chill, you would run a calibration by pouring both wedges and the cups, then run the results though a regression analysis for the equation to put into MeltLab. Generally you would pour the wedge first, followed by the tellurium cup because the boiling would cause it to lose some temperature, and finally the plain cup.

One unique application we found for dual cup was white iron. In this case, the foundry needs a slight temper in the iron, but not too much. This results in a little graphite showing up in the iron and results in a very hard iron, but one that is slightly less brittle. Typically the wire iron foundries were looking for ½ to 1 degree C separation.

With grey and ductile irons, you could easily experience 10 to 30 degrees C separation between the white and grey (graphite containing) curves. Greater separation causes lesser chill and softer iron. Because the overall chemistry has an effect, it is generally a good idea to generate a chill equation for each grade of iron. This allows for the effect of different levels of pearlite stabilizing elements such as chrome and manganese in grey iron, as well as the ferrite forcing elements such as magnesium in ductile iron.

We have now moved that technology over to the version 5 of MeltLab to give an extra boost to iron foundries needing information on their process.

DualCup analysis for a heavy section ductile iron



Red curve on left is tellurium cup, red curve on right is plain cup, and the light green curves are from the other cup.

Dual Cup Analysis for Iron – October 2010

Thermal Analysis Measurements Basic and Advanced MeltLab values[1]

Chemistry/Tellurium Cup	Grey Iron Microstructure	Ductile Iron Microstructure
C.E.[2]	C.E.	Graphitic Liquidus
Carbon[3]	Liquidus	Austenitic Liquidus
Silicon[4]	Eutectic	Graphitic C.E.
Liquidus	Solidus	Austenitic C.E.
Eutectic	Max Temperature	Eutectic Undercooling
Solidus[5]	Carbide Index[6]	Eutectic Growth Temperature
Oxides[7]	Oxides	Eutectic Recalesence
Tramp Index[8]	Shrinkage[9]	Solidus
Max Temperature[10]	Freezing Ranges[11]	Solidification Mode[12]
Carbon Addition[13]	Inoculation Addition[14]	Primary/Secondary Graphite[15]
Silicon Addition	Graphite Activity[16]	Graphite Activity
Steel Addition[17]	A-Flake estimate[18]	Nodularity estimate[19]
Saturated Carbon[20]	Eutectic Gas[21]	Pearlite/Ferrite by chemistry[22]
Superheat[23]	Tramp Index	Shrinkage
	Eutectic Undercooling[24]	Tramp Index
	Eutectic Growth Temperature[25]	Carbide Index
	Eutectic Recalesence[26]	Eutectic Gas
	Superheat	Max Temperature
		Superheat

Dual Cup then combines the chemistry/tellurium column with either the grey iron microstructure or the ductile iron microstructure column. In addition, by comparing the chemistry eutectic temperature with the eutectic undercooling, we get to calculate the chill as well, giving us not only the best of both worlds, but an added bonus.

In the end-notes, I have tried to describe most of the arrests that may be unfamiliar. If you have any questions, please email me and I will be glad to explain almost everything. Sorry competitors, but our smoothing technique that allows us to get down to the 5th derivative remains a trade secret – no explanations on that subject.

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[1] Basic and Advanced are two different levels of analysis offered by MeltLab. Basic includes all the test values commonly offered by our competitors, Advanced offers all the Basic values plus all the values commonly reported by research papers as being beneficial. There is a cost difference between the two.

[2] C.E. or Carbon equalivant is determined by the liquidus number. It is a measure of the fluidity of the iron, and should not be confused with published equations for calculating C.E. by chemistry. Calculating C.E. by chemistry is an attempt to *imitate* the C.E. by liquidus temperature. The Liquidus temperature method is the real thing.

[3] Carbon is calculated by an equation of the form Carbon = (k_1 * Liquidus) + (k_2 * Eutectic) + k_3 where the "k" values are calculated constants. This value is typically a better value than a spectrometer can produce, and should be consistent with combustion analysis within 0.03 to 0.05 percent. A common cause of larger disagreements is segregation in the combustion carbon standard. Please shake the standard bottle before using it to calibrate your combustion carbon instrument.

[4] Silicon can be calculated either by the AFS method Si = (k_1 * (C.E. – C)) + k_2 or by the BCIRI method Si = (k_1 * Liquidus) + (k_2 * Eutectic) + k_3 where the "k" values are calculated constants. The first equation is solved by a bivariant regression, and the second by a trivariant regression of the spectrometer lab and MeltLab data.
[5] Solidus, sometimes called the end of freezing, is where the grain boundaries freeze off. The temperature is controlled by the degree of micro-segregation or the amount of tramp elements in the grain boundaries. Irons with lower total tramps have a higher solidus.
[6] The carbide index is a measure of how strong the carbide arrest is. We are currently working on the next level of thermal analysis - ***Expert*** - that will use integration to measure the actual percent carbides. This is part of my paper submitted to AFS for the 2011 Casting Congress, and the feature will be ready by that time.
[7] Oxides in molten iron will react with the inoculation materials and/or the magnesium treatment materials, reducing their effectiveness. There are no oxides in treated ductile iron, as the magnesium removed them all.
[8] Tramp index is a measure of the low melting elements being segregated into the grain boundaries: often referred to as micro-segregation. This has been reported to affect cold fracture strengths of ductile iron and austempering of ductile iron. I believe that there is probably more to be learned here. This is an area open to more research.
[9] Shrinkage is measured both directly from an actual shrink event and from the residual stress in the iron at solidus. At times, the stress is relieved either by forming a shrinkage void or by a suck-in. These the software properly recognizes as an iron being very shrinkage-prone. This is much more common in ductile iron than in grey.
[10] Max temperature should be watched to keep this value below the melting point of the thermal couple. A high max temperature can lead to cup failure and missed analysis. On the other hand, a low sampling temperature may miss the liquidus and pre-liquidus arrests, and if sampled from a furnace on its initial melt-in below 2550 F/1400 C, may miss seeing the total silicon value, as the silicon may not be totally dissolved yet.
[11] The two freezing ranges are from liquidus to solidus and from eutectic to solidus. Larger ranges increase the difficulty in feeding iron.
[12] Solidification modes include hyper-eutectic, eutectic, and hypo-eutectic as well as a special case of a combination of hyper- and hypo-eutectic mode. Hyper-eutectic is prone to shrinkage defects in thicker section size and makes solid risers. The hyper/hypo-eutectic mode is generally a disaster, with massive shrinkage and poor feeding and is commonly referred to as carbon flotation.
[13] All addition calculations are to achieve one of three possible aims: correct to in-range, correct to the center of range, or to correct the next charge. This aim can be decided by the user through software configuration.
[14] Inoculation addition is based on the recalesence value for grey iron.
[15] Primary and secondary graphite are the larger and smaller nodules seen in the microstructure. We ratioed the energy of the eutectic, both before and after the eutectic growth temperature, to derive this value. Larger secondary graphite values are preferred to reduce shrinkage.
[16] Graphite activity is the noise in the 5^{th} derivative, caused by the explosive growth of the graphite in both grey and ductile microstructure thermal analysis. In both cases, less desirable graphite generates more variation in the 5^{th} derivative. A-flake and nodularity calculations are based on this measurement.
[17] The Steel addition is added in to dilute an element. Sometimes this is not practical, but gives the user an idea of how far off the chemistry is. Another option is for the computer to calculate changes to the next charge. In that case, negative additions are allowed as in -5 Silicon would mean removing 5 units (kilograms or pounds) from the next charge.
[18] A-Flake is based on graphite activity, and this number improves with inoculation.
[19] Nodularity is based on the graphite activity value. Vermicular graphite grows more rapidly than spheroidal graphite and increases the roughness of the 5^{th} derivative.
[20] Saturated Carbon is a measure of the C.E. verses the theoretical eutectic C.E. of 4.33. A value less than 1.0 is less than the eutectic value, and a value greater than 1.0 is greater than the 4.33 value. This measurement is commonly used in Europe, but not so well known in America.
[21] Eutectic Gas can be a problem for thermal analysis by causing a gas bubble to form around the thermal couple and insulating it from the iron. Most of the time, gas is a minor problem, but with some irons it can be a major problem both with thermal analysis and with the castings.

[22] The pearlite/ferrite estimate is based on the amount of carbon retained in the iron chemically (total carbon – carbon in graphite). It does not work if the castings are air quenched or if the cup is not properly filled and the cup cools too quickly.
[23] Superheat is the maximum temperature minus the liquidus temperature, or if there is no liquidus, the eutectic temperature. The superheat assures an accurate analysis of the liquidus and needs to be at least l10-15˚ C.
[24] Eutectic undercooling is caused by the lack of sufficient nucleation sites in the iron. This value is the lowest temperature found during the eutectic arrest. Subtracting the undercooling value from the growth temperature value produces the degrees of recalesence.
[25] The eutectic growth temperature is the highest temperature reached during the eutectic arrest. This is generally also the true eutectic, but insufficient iron in the cup may cause this temperature to be lower than it should be, due to rapid cooling.
[26] See the notes on eutectic undercooling for more information. The higher the recalesence number is, the less inoculated the iron is.