Understanding Thermal Analysis of Iron
铸铁热分析的理解

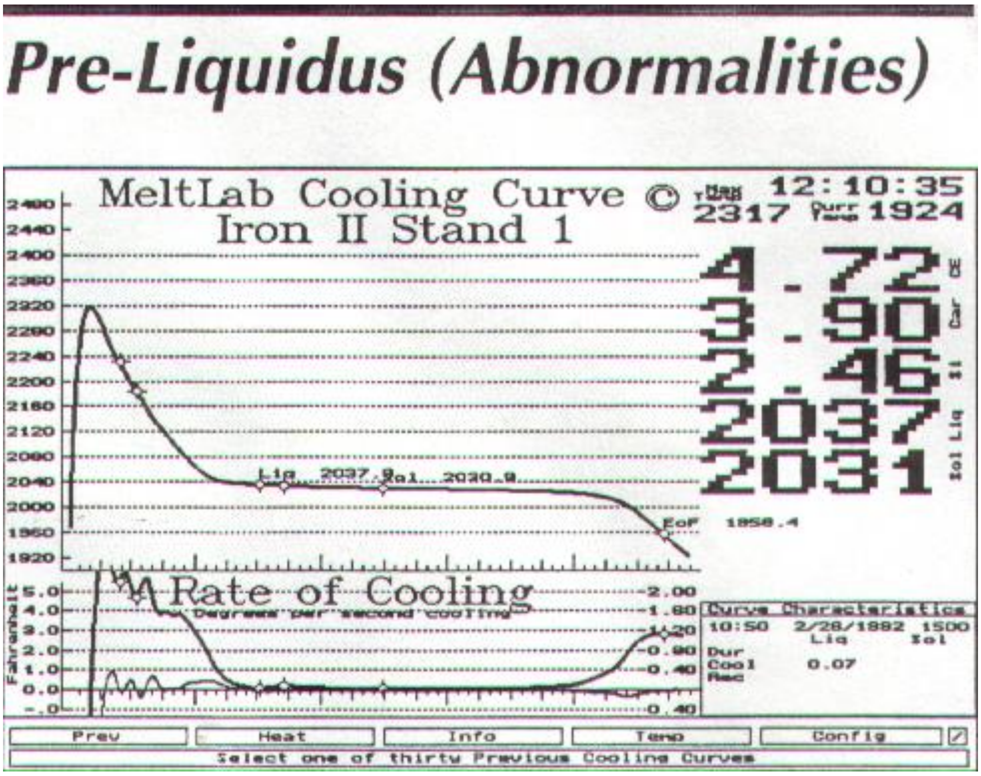
By David Sparkman Foundry Information System 1992

With the arrival of new 16 bit Analog to digital converters, computers, and computer enhancement software, it is now possible to see and measure events within the solidification of iron samples that can be used to approximate chemistry, chill, soundness, and micro structure. The purpose of this paper is to discuss the different parts of the thermal analysis cooling curve and how they relate to the final castings. I have limited the discussion to the hypo-eutectic irons that are most commonly used in malleable, gray, and ductile irons.
随着 16 位模数转换器，计算机和计算机增强软件的到来。现在可以看到和测量铁样近似的化学成分、激冷和微观组织的事件。本文的目的是讨论热分析的冷却曲线的不同部分与其相关的最终铸件事宜。我可以有限地讨论到对于大部分的可锻铸铁、灰铁和球铁的亚共晶铸铁。
First, a disclaimer is in order. What is discussed in this paper is related to relative changes in the thermal analysis and is not an absolute predictor. This simple means that each foundry must do their own homework to find out what ranges work best for them. No foundry should expect ranges from another foundry to work in their foundry.首先为了免责，本文中讨论的是涉及到热分析变化，不是绝对的。

There are many reasons for these differences. One main reason is that spectrometer silicon’s on older instruments may have a gage error of up to 0.15, and a similar calibration error. Newer instruments may reduce that error to 0.05. That means that foundries may disagree on silicon by as much as 5, 10 or even 15 points. A second major problem is the rate of cooling, due to air movements around the cup, may vary widely between foundries. There are several other minor reasons, but they all boil down to one conclusion: each foundry needs to do their own homework to determine equations and operating ranges. 对于这些差异有许多原因，其中一个主因是老的光谱仪分析硅会有一个仪表误差达到 0.15，和一个类似的校正误差。较新的仪器会降低误差至 0.05. 那意味铸造厂将不同意硅的含量 5、10 甚至 15%。第二个主要问题是冷却速率，由于样品周围的空气流动，各铸造厂之间会宽泛的变化。还有些其他的次要原因，但他们都归结一个结论：每个铸造厂他们都需要做自己的功课去决定方程式和操作范围。

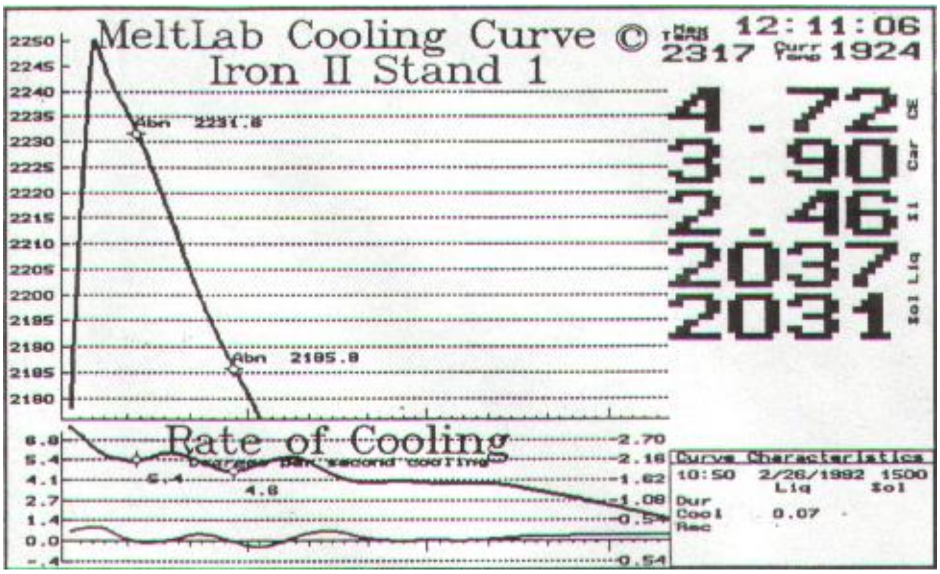
To lend order to this discussion, I will divide the thermal analysis curve into various parts of interest and disinterest, and discuss the importance of each part. I will be defining each part by the characteristics of the temperature plot, and the behavior of the rate of cooling (inverted first derivative), and the second derivative(导数).要为了讨论，我要将这热分析曲线区分成各种感兴趣和不感兴趣的各种部分。我要定义各种温度曲线的特性，和冷却速率的行为(倒一阶导数)，以及二阶导数。

The major parts of the thermal analysis curve are described as the pre-liquidus section(预液相部分), the liquidus arrest, the dendritic growth section (枝晶生长部分), the eutectic solidification area, the end of freezing point, and the austenitic transformation area. Different chemical and physical reactions occur during each part of the curve. These reactions play a significant part in the final structure of the casting. We will consider the thermal curves for tellurium treated, and untreated thermal analysis cups. 热分析曲线的主要部分是被描述为预液相部分，液相线的捕捉，和枝晶生长部分，共晶凝固区域，凝固点结束和奥氏体转变区域。不同的物理化学反应发生在曲线的每一个部分。这些反应在铸件的最终的结构上发挥了显著的部分。我们要考虑碲处理和没有碲处理样杯的热分析曲线。



Figer1 (Near Eutectic Gray Iron 近共晶灰铸铁)

This is the section starting from the highest temperature down to just above the liquidus arrest. During this time we may experience some noise from the cup, especially if we are using a tellurium cup with the tellurium in the form of a bead. These beads can absorb moisture and cause boiling and spitting in the iron. In addition, the beads contain materials to promote an abnormally strong liquidus so the older equipment could reliably detect it. I prefer the cups with a tellurium(碲) wash. Since, they are quieter in this region the real arrests are easier to determine. 这部分是从高温冷却至液相线的捕捉，在这阶段中，我们会经历到来自样杯的噪音，尤其假如我们正在使用含碲珠形式在杯底的碲杯，这些珠子能够吸收水分和在铁中引起沸腾和噼啪相。此外，珠子含有的材料会提升异常强烈的液相。因此旧设备能够地探测到，我更喜欢碲的洗杯。一直以来，他们都在这个地区真正捕捉到容易确定的噪音。



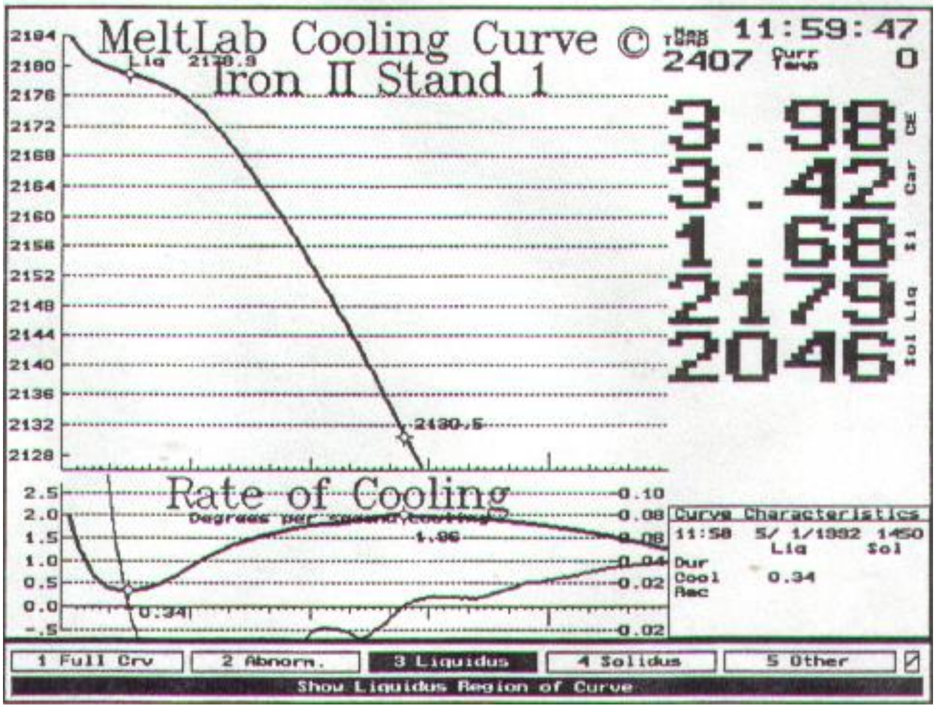
Figer2 (Abnormality Section of Cooling Curve 冷却曲线异常)

The arrests in this area are oxygen and possible sulfur related. Cupola shops will see more of these arrests when the coke bed gets low and the slag indicates oxidizing condition 1. These arrests have also been occasionally seen when melting rusty scrap in coreless induction furnaces. Common temperatures for these reactions seem to be 1195-1200C, and 1170-1180C, or 2155-2165F, and 2138-2156F. Some possible reactions within iron at this temperature involve Manganese Sulfides and Oxides. 这方面的捕捉是氧和可能硫相关的，当底焦降低和渣显示氧化时使用冲天炉的会看到更多的这种现象捕捉。1）这种捕捉在无芯感应炉熔炼生锈的废料是也偶尔遇见过。似乎是这些反应的常见温度 1195-1200C 和 1170-1180C 或者 2155-2165 和 2138-2156F，一些可能的反应在此温度下与铁涉及到硫化锰和氧化锰等。

The abnormality reactions are much weaker than the major arrests and their duration's are short and far less energetic than the liquidus arrest. In an arbitrary fashion, we have chosen to define the existence of one of these arrests as when the rate of cooling has fallen away from the maximum, and the second derivative passes through zero in a positive direction. Lesser arrests may have second derivative that come close to zero. At the moment, we are concentrating on only the larger, stronger arrests.

Liquidus And Austenitic Arrest

Liquidus And Austenitic Arrest

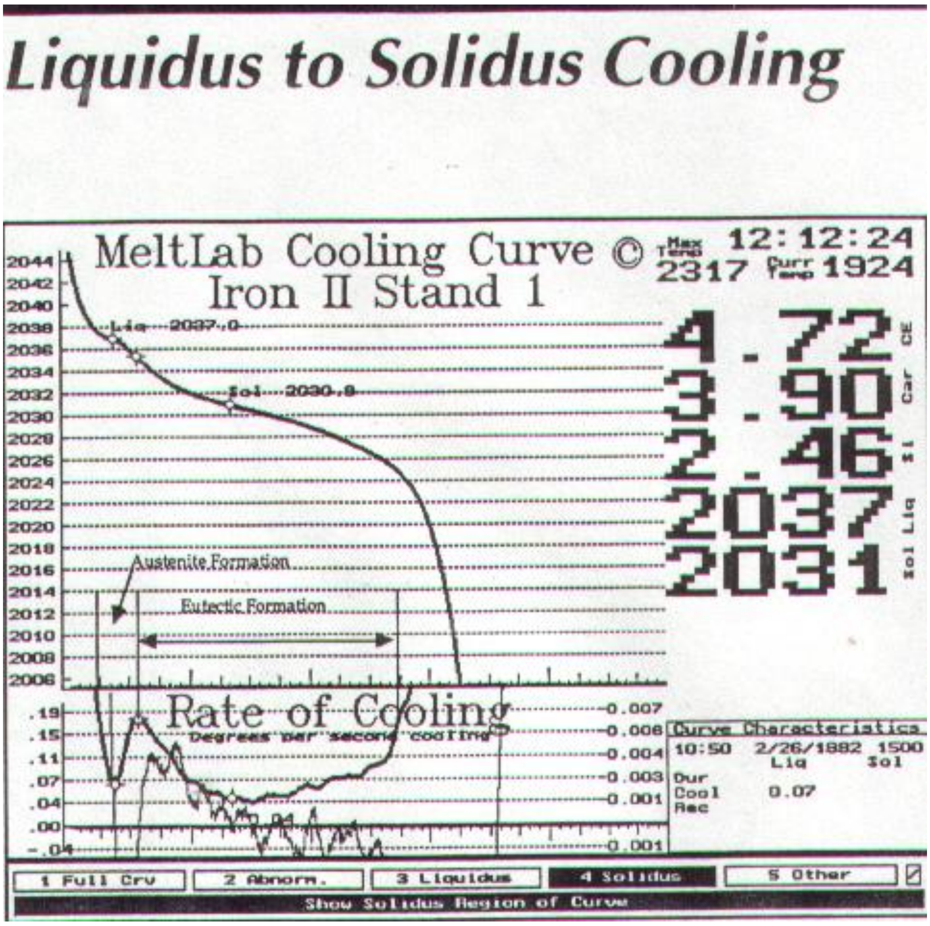


During the liquidus arrest, Austenitic dendrites begin to form. The strength of this reaction depends on the number of nuclei available to start crystals. It is believed that the austenitic cells and their growth contribute to the final physical properties of the iron, so good nucleation is important. Unfortunately, one manufacture of cups adds ingredients to the tellurium drop they use to promote a strong liquidus reaction. If these cups are used, then no conclusion can be drawn from the rate of cooling and duration of the liquidus. On the other hand, the tellurium washed cups are repeatable, and do not seem to significantly change the nature liquidus arrest.

The liquidus temperature determines the carbon equivalent. For our definition of the liquidus, we take the temperature of the lowest rate of cooling during the liquidus arrest. The mathematical definition is when the rate of cooling is within the expected range for liquidus and the second derivative passed through zero. This has been found to be correct for base, and treated gray iron using either tellurium or non-tellurium cups. In addition, it seems to hold well for base and final ductile iron. Chaudhari and Heine report “insignificant change in the austenite liquidus temperature (TAL)” for magnesium treated hypo eutectic gray iron.

An interesting application of the liquidus duration is in predicting nodularity in Ductile Iron. This was first achieved by Heraeus Kunzer with the Multi-Lab QuiK-Cup. Heraeus uses a technique to measure the relative thermal conductivity of the soldtying iron and “relates this to the morphology of the graphite in the iron.” Private research indicates that, with the newer thermal analysis equipment, an accuracy of 5% nodularity may be achieved. Research is continuing in an attempt to improve the accuracy further. Like the silicon calculation that is mentioned late, the nodularity calculation is site specific and can change with the grade of iron, and of course, section size. Nodularity has also been predicted based on the solidus reaction. See the section on Solidus.

Liquidus to Solidus Cooling

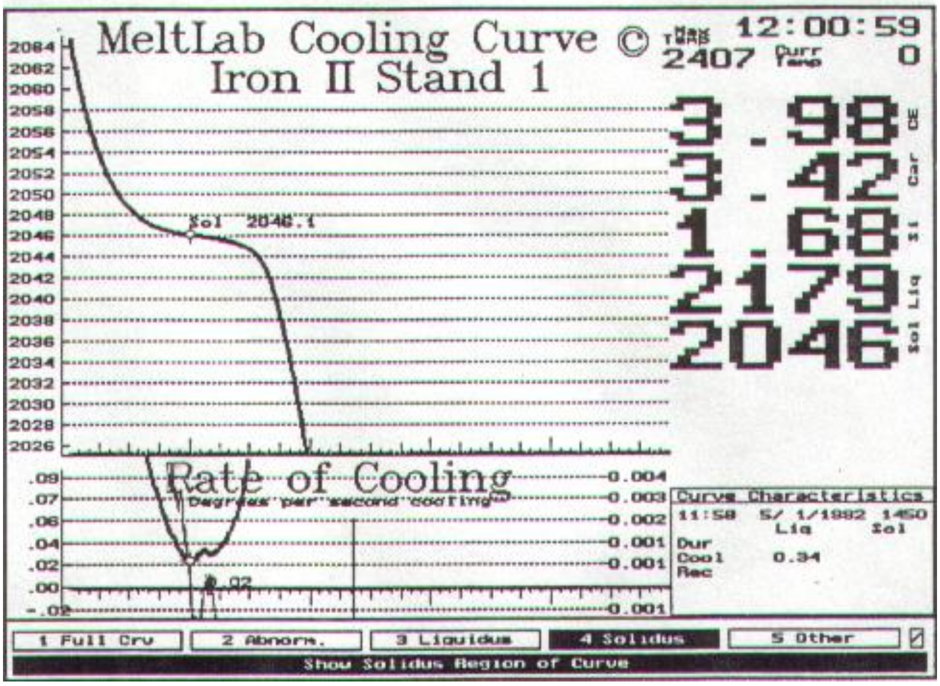


The area above the rate of cooling and the natural cooling is proportional to the amount of solidification. If the area before and after the maximum Rate of Cooling between Liquidus and Solidus is ratioed, then the percentage austenite vs. percentage eutectic can be estimated. The area before the maximum Rate of Cooling is the austenite, and the area after is the eutectic.

During this period of time, the austinetic dendrites are growing into the sample. This growth generates heat so the higher the rate of cooling, the lower the growth rate. According to Glover, Bates and Monroe "Austenite dendrite interaction was shown to be a major factor in determining the tensile strength of the irons tested." Hence, a lower rate of cooling will promote a stronger iron, if everything else is equal, but this may also promote D flake.

Ekpoom and Heine suggest that and inflection during this phase of cooling can indicate mottle in malleable iron.

Eutectic Arrest, Bulk Arrest or Solidus



Solidus is common name for this arrest, although we will see later that End of Freezing point is the point when the casting become completely solid. With tellurium during this phase, iron carbide and possibly a small amount of austenite is formed. Without tellurium present, this phase forms graphite, ferrite, and iron carbide. We will occasionally see strong spikes or dips during the solidus that as of yet are not completely explained. In some of his research in Ductile Iron Dr. Loper suggests that, “the shape of the cooling curve following the bulk arrest (Solidus) can be identified with the degeneration of the normal spheroidal growth process into one causing non-spheroidal forms. “Research in the 70’s produced a system of visual checks that would relate the release of heat during the first part of solidification to the percentage nodularity. An early recalescence indicated nodularity, while a late recalescence at a lower remperature indicated flake graphite. This effect can also appear in gray iron.

Occasionally there will be an unexpected rescalescence in a tellurium cup. This can happen if there is undissolved graphite in the molten iron from a late carbon addition, from a graphite washed sampling spoon, or from a cold melter that has not yet reached enough temperature to dissolve the carbon addition. Magnesium treated Ductile Iron will show recalescence unless the sample cup contains enough sulfur to neutralize the magnesium. If there is recalescence, the carbon and silicon will be incorrect. One degree of recalescence will change the carbon by about 0.01, and the silicon by about 0.03 from what should be reported.

From the liquidus and solidus temperature of a tellurium treated sample, the carbon and silicon can be approximated. The equations for this approximation are given in several papers by Heine, and BCIRA. The equations are affected by the amount of phosphorus, manganese, tin, and chrome present. Individual foundries should adjust the slope and offset of the silicon equation by experimentation to compensate for these other elements. It may also be necessary to have a separate silicon equation for each major type of iron.

DUALCUP ARRESTS

Recalescence(复辉，再炽热) in an untreated sample tells a great deal about the inoculation of the iron. The greater the recalescence, the more inoculationp the iron requires. Well-inoculated iron will typically have a recalescence from 6 to 10℉or 3 to 5℃. Uninoculated electric melted iron will range from 14 to 18℉or 7 to 9℃. Cupola melted iron may be lower then electric melted iron if the oxidation is not too bad in the cupola. Regardless of the source of the iron, it's present condition, and present inoculation requirements can be determined buy the recalescence.
In treated Ductile Iron, Chaudhari suggests that a recalescence of more than 15℉ or 8.3℃ "is associated with degenerated graphite micro-structure".

Dual Cup Solidus Arrests, slow recalescence

Van der Perre suggests that 100% A Flakse is achieved at 5℉, 3℃ and less, though he offers no scaling on his graph. He also related the ratio of the recalescence of uninoculated with inoculated iron to predict eutectic cell numbers.

Chill is another important characteristic of Cast iron. Chill occurs when the iron becomes undercooled enough to form carbides instead of Graphite, and Peartile. The temperature at with carbides form moves with silicon and is the same temperature at which the tellurium solidus occurs. Degrees undercooling is generally a negative number and is the distance between the minimum recalescence of the untreated curve, and the carbidic (tellurium induced) solidus arrest.

Since the depth of chill depends on chemistry, casting thickness and inoculation, and excellent way to control chill is by controlling the degrees of undercooling. Since the carbide eutectic moves with silicon content, the ideal situation is to pour both a treated and an untreated cup. From the treated cup, which reports a silicon, the carbide eutectic can be calculated. From the untreated cup the undercooling temperature is determined, and from both results, the degrees of undercooling can be calcaulated. Since foundries differ on their silicon analysis, I can offer no guide for what a good degree of undercooling number is. But shifts from normal ranges do indicated chill problems. The ranges for this undercooling number will need to change based on casting thickness and other factors. This technique offers greater accuracy than the normal chill test, and is a calculation instead of a subjective measurement.

Carbides can form in the casting in two ways. First, if the initial undercooling of the Solidus dips down below the Carbide Eutectic temperature carbides can freeze out of the liquid. Chill wedges force this by extreme cooling of one edge of the sample. Thin castings with sharp corners will generally have at least a small amount of chill in these corners even with good practice. The second type of chill happens when the temperature at the end of the Solidus reaction starts to fall off and the End of Freezing has not been reached. This accounts for the small intercellular carbides we sometimes find in micros. While in practice it may be impossible to keep the tail of the solidus curve above the carbide eutectic temperature, good foundry practice will keep the carbides microscopically small and few enough to prevent any adverse effect in machining. A curve that is well above the carbide eutectic and then rapidly falls off in temperature at the end of the solidus is less likely to produce significant carbides because most of the metal has completed solidification.

Important thermal analysis research is being conducted at the University of Wisconsin, USA in shrinkage prediction for ductile castings. While this research is being conducted with the best of intentions, the resulting equations of this research are complex enough to make one wonder if there is not a simpler solution to be had. The shrinkage not being caused by sand, casting shape, cooling rates, risering and gating practices, is generally caused by the dendritic austenite blocking feeding paths, and the length of time required for the bulk solidification to occur. This is determined by inoculation, oxidation, and other factors that are small and difficult to measure in the lab. Much of this research was conducted using the tellurium bead cup that alters the size and shape of the liquidus arrest. For this reason, I believe the researchers did could not find correlations with the austenite cell formation suggested by theory.

End of Freezing

A common mistake is to think that the solidus is the actual point of final solidification. The final freezing of the grain boundaries can happen 40 to 120℉ or 20 to 60℃ later. This difference is important to the soundness and strength of the castings. After most of the heat of solidification has been used up, the low melting phases in the iron are still liquid, these solutes will have been forced to the grain boundaries where they finally freeze in concentrations more than 100 times their normal levels. These phases may include phosphorus, tin, antimony, and lead compounds of iron. If these phases concentrations are high, then the end of freezing temperature will be lower. The difference between the solidus (eutectic freezing) temperature and the end of freezing temperature is then an indicator of the concentration of these low melting point phases.

This inflection is important for two reasons. First, feeding cannot occur at this point. The dendritic austenite and eutectic crystals occupy 99.9% + of the casting. If the delta freezing temperature is too large, then micro-shrinkage voids can occur in the grain boundaries. In addition, these low melting phases are not good for strong physical properties, and large delta freezing may lead to lower tensile strength, yield strength and percentage elongation.

The end of freezing point is an unusual endothermic (energy absorbing) reaction. A theory to explain this may be relate to the degree of disorder in the grain boundaries that freeze more like glass than like metal. In addition, if there are stresses and even voids being formed from the liquid, then energy would be absorbed. This would suggest that the height of the Rate of cooling peak and the area underneath it may also indicate the degree of micro-shrinkage. 凝固点是一个不寻常的吸热反应（能量吸收）。

Austenitic Transformation

This is the point between 1450 and 1400℉ when the austenite is transformed into a form of iron carbide. It may be as pearlite, martinsite, bainite or mixtures. The transformation is as yet hard to detect. In a normal sample cup, this transformation may take as long as 10 to 15 minutes to occur. Problems occur when the cup disintegrates and falls away from the sample exposing it to air on one side or more. This causes a noticeable change in the rate of cooling, and can confuse the analysis if it happens at an inopportune time. For this number to become a useful tool, the cup design will need to be rethought. 这个温度点在1450-1400℉之间当奥氏体转化为碳化铁的一种形式。它也许是珠光体，马氏体，贝氏体或者其混合物, 这种转化难以探测的。在一个正常的样本里，这种转变可能只要10-15分钟发生。这将导致在冷却速度显着的变化，如果它发生在一个不合时宜的时间，可以混淆的分析。

Inflection Points 转折点

The following simplified definitions are offered as an alternative to the confusing and often cryptic abbreviations in the literature. We hope this will serve as a foundation for future discussions.

Abnormality	A strong inflection above the liquidus that is not system noise. It is characterized by a second derivative approaching or exceeding zero.
Start of liquidus	The Minima in the second derivative just before the actual liquidus after the first derivative(导数) Rate of Cooling has fallen below a given limit that characterizes the grade of iron and the thermal analysis system. For Cray Iron with small cups, this would be about 4C.
Liquidus Arrest	The period of time between the Start of Liquidus and the End of Liquidus. During this period, austenite is formed in the iron.
Actual Liquidus	This could be any point during the liquidus. For the sake of accuracy and uniqueness, we will call it the point of the minimum rate of cooling during the liquidus arrest. With the older, less precise equipment, this precision was not possible. The rate of cooling at this point can be an indication of the degree of austenite formation if the cup has not been treated with materials to change the liquidus.
Min. Liquidus	This is the lowest liquidus found before recalesence is detected in the liquidus. It is the same as the actual liquidus point.
Max. Liquidus	This is the maximum temperature found during recalesence in the liquidus. This recalesence is generally caused by additions made to the cup by the manufacture. Some of the older thermal analysis equipment required a strong liquidus for a correct reading.
End of Liquidus	This is the maxima in the rate of cooling that occurs between the liquidus and the solidus. At this point the formation of Austenite has slowed or stopped.

	Gray iron typically has more heat being generated at this point than ductile iron has. Iron high in chrome and other austenite forming alloys will show only a minor inflection for the end of liquidus. Austenite may continue to form below this point, but the eutectic material may slowly form in localized areas. It is suspected that graphite is the main material formed during this period.
Start of Solidus	This is the minima in the second derivative that occurs just before the start of the solidus arrest. It indicates that the drop into the bulk freezing (solidus) arrest is starting to level off. Beyond this point, eutectic material (graphite, pearlite, and ferrite) begin to form. Some people prefer to use this value for their solidus calculation because of its uniqueness.
Min. Solidus	This is the minimum temperature before recalesence during the solidus. This is alos the undercooling temperature that can be compared against the carbidic arrest of a tellurium cup to calculate the degree undercooling (a measuere of inoculation).
Max. Solidus	This is the maximum temperature during recalesence in the solidus. The degrees recalesence is calculated from comparing this temperature with the minimum solidus.
Zero Solidus	This is where the second derivative first passes through zero during the solidus arrest. Because this comes from a gradual drift into zero, this number may move around by as much as a degree causing a corresponding change in the carbon and silicon calculation. Some people prefer to use this value for their solidus calculation, though it may not be as consistent as the start of solidus.
End of Solidus	This is the minima in the second derivative just before the end of freezing. At this point, heat is no longer being generated by the solidus arrest.
End of Freezing	This is the maxima in the rate of cooling following the solidus arrest. At this point the grain boundaries have solidified.

Reference Section

In addition to the above listed articles, the following published and privately published articles are recommended for further study：

1 James M. Frost, Doru M. Stefanescu “Melt Qulity Assessment of Spheroidal Graphite Cast Iron through Computer Aided Cooling Curve Analysis”, 96th AFS Castinh Congress, Milwaukee, Wisconsin, May 6th, 1992.

2 M. Booth “Thermal analysis for composition determination of gray cast iron”, British Foundryman, March 1983.

3 Doru M. Stefanescu “Cooling Curve Analysis as applied to cast irons and aluminum alloys” handout from lecture.

4 A. Alagarsamy, F. W. Jacobs, G.R. Strong, R. W. Heine “Carbon Equivalent vs. Austenite Liquidus：What it the correct relationship for cast irons?” AFS Transcations 84-31.

5 R.W. Heine “Carbon, Silicon, Carbon Equivalent, Solidification, and thermal analysis relationships in Gray and Ductile Cast Irons” AFS Transcations 73-82.

6 C.R. Loper Jr., R.W. Heine, R.W. Reesman, B.H. Shah “Thermal analysis of Ductile Iron” AFS

Transcations 67-41.

7 G.F. Sageant “Thermal analysis of magnesium-treated cast iron” BCIRA report 1341, 1979.

8 G.R. Strong “Thermal analysis as a ductile iron molten metal processing evaluation tool” AFS Transcations 83-94

9 R. Monroe, C.E. Bates “Thermal analysis of ductile iron samples for graphite shape prediction” AFS Transactions 82-131.

Footnote Section

1 Based on unpubilished experiments at Sturgis Foundry, Sturgis Michigan during 1991.

2 M.D. Chaudhari, R.W. Heine “Principles involved in the use of cooling curves in Ductile Iron process control” AFS Transactions 74-96.

3 Multi-Lab QuicK-Cup (trade marks of Heraeus Electro-Nite) information brochure EN MLQ1-30-01.91 E.