Micro Event Analysis of Cooling Curves

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With the advent of high speed personal computers, it is possible now to see micro events happening in the cooling curves of metals, and to rapidly make calculations that used to be impractical. This paper will show examples of measuring gas and shrinkage forming in thermal analysis curves as well as how ductile iron nodularity can be seen and measured though micro-event analysis.

Overview

Thermal analysis is the art of looking for changes in the rate of energy production and energy loss as a material changes phases. For the foundryman, this usually is seeing how the metal solidifies. There is loss of temperature by the metal loosing heat by radiation and conduction, and there is energy being produced as the atoms of the metal take on the more organized structure of a solid.

But there are also very small events occurring as well as for example: gases, shrinkage, and stress adsorb energy through their endothermic forming of interior surfaces, and strain in the grain boundaries. These increase the rate of cooling. Other reactions, such as the growth of dendrites in iron and hypo-eutectic aluminums produce rapid heat generation. The degree of speed involved tells us about such things as dendrite spacing, degree of inoculation, and possible feeding problems.

Oxide arrests come from the formation of mullite in iron as the dissolved oxygen held by silicon dioxide is released to form $FeO{\cdot}SiO_2$ compounds. The degree of oxidation will determine how poor the inoculation recovery or the magnesium recovery will be. And of course, carbides and D and E-Flake may form towards the end of the eutectic arrest, if the iron is not fully inoculated.

Another aluminum crystal structure that may show up as a micro-arrest is the undesirable Beta crystal. Detection of interstitial crystalline structures would be a great benefit, and bring thermal analysis close to being a substitute for microanalysis, or at least a quick check on microstructure.

Tools and Methods

A library of thermal analysis curves made over the last 15 years of various types of iron, grades of aluminum, and copper-phosphorus alloys have been made available by customers. These curves preserve raw unsmoothed thermal analysis temperature curves at between 3.7 samples per second and 6.0 times per second. Newer data collected at 10 samples per second are also available. This library provides the means of finding

examples of defects and problems and designing algorithms to pick out these micro-events which was then combined into a run time program.

We used both ElectroNite and Minco thermal analysis sand cups for iron and copper based samples, as well as the Pechine designed sampling stand for aluminum and copper based samples. We used the existing MeltLab analog digital converter box to convert signals from the molten metal samples into computer format. In the new system, we had to deal with limitations of the Microsoft XP operating system. In particular we were limited to 100 readings per second divided by the number of inputs. The older software was capable of up to 240 readings per second. We used this limitation for our advantage by putting the system on constant read, and then averaging the readings for $1/10^{th}$ of a second for each input.

The granularity of the measurement is about $1/20^{th}$ of a °C, and the calibration accuracy is about +/- 0.1 °C. The calibrator is only calibrated to the nearest 0.1 °C, and the thermal couple wire bias is reported by one company to about 0.1 °C. The other major manufacturer does not make it a practice to report wire bias, but say their wire is +/- 1.1 °C. No statistical description was applied to this bias. It was therefore possible to correct for wire error from the first, but not from the second. Using the sum of the square of the errors we get Sqrt (0.05^2 + 0.1^2+0.1^2 + 0.1^2) = Sqrt (0.0325) = +/- 0.18 °C for the first and Sqrt (1.2325) = 1.11 °C for the second company's products. Wire matching is a technique that both companies use to minimize the wire bias, but without reporting the resulting bias to the customer, there is a lack of responsibility of producer to customer.

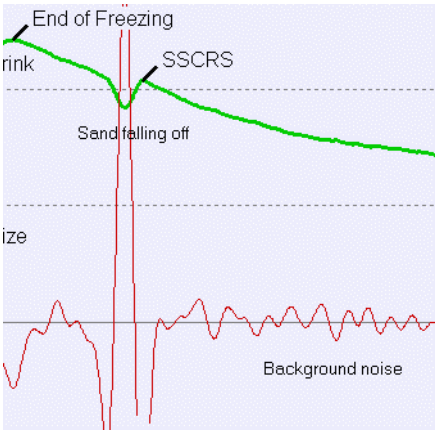
We chose to smooth the data as little as possible so as to avoid rounding off the corners of arrests, and we chose to calculate down to the 4^{th} derivative for certain arrests. The results were very good as we could see very small events, and even had to tell the computer to overlook very tiny events that were not of consequence. For example if a small but visible gas event registered a 20, then events of 1 and below which only the computer could see were ignored.

Smoothing as been a sore point for many researchers, and to some degree, the methods used remain a trade secret. We have experimented with several techniques including multiple pass, clipping, variable sample size, etc. The result of our many experiments can be summed up in 1) Shield the wiring to prevent noise from getting into the system. 2) Use two wire differential thermal couples. 3) Sample reasonably fast, but not so fast as to introduce error. 4) Calculate the derivative using a sample size that matches the noise of the system.

Most papers presented to AFS graph the first derivative; many place the plot on top of the temperature plot. We have always chosen to plot the cooling rate which is the first derivative inverted. This preserves the terminology of "Cooling Curve" and the logic of a common foundryman over the logic of a mathematician. The cooling curve and the cooling rate are then not so confusing to a person untrained in higher mathematics.

Degree of noise reduction

Noise reduction can be seen by comparing smoothed and raw data in a visual format. But mathematical comparisons can also be made in a fairly simple way. If a section of the curve can be found that is flat, we can use a standard deviation calculation on the data points as a measure of the noise. Since flat parts do not commonly occur on a thermal analysis curve, a derivative will do. Typically when no micro-events are occurring, the third derivative will be a reasonably good indicator of non-filtered noise. The area right after the SSCRS point is generally a good place to check for noise. The only "event" that commonly occurs here is when the cup deteriorates and sand falls off which increases the cooling rate.



The meaning of derivatives

As an old math teacher said, distance, velocity and acceleration, velocity is the derivative of distance, and acceleration or deceleration is the derivative of velocity. Each inflection point of the curve can be approximated by some change in acceleration of deceleration in the rate of one of the derivatives. When a derivative reaches a maximum or minimum acceleration, the next derivative is passing though zero and changes its sign. This change in sign is very easy for a computer to test. In fact, the program we designed tracks about 100 times where one of the four derivates crosses zero, then sorts out which cross over is which arrest, all in the blink of an eye. The result is about 25 to 30 important points on the curve where something is changing. From there, rules based on the metal type and the state of the metal are applied, and the micro-effects are calculated.

For example, in a metal with a weak liquidus (base iron, or hypo-eutectic aluminum), the liquidus temperature is defined as the temperature of the metal when the rate of cooling reaches a minimum, and only when that minimum rate of cooling is below 1 °C. This avoids oxide arrests in iron. So the computer rule is:

> If the metal type is Base Iron or hypo-eutectic aluminum,
> And the liquidus has not yet been found
> And the Rate of cooling is below 1 °C
> And the second derivative is passing though 0
> Then this point is the liquidus and no other liquidus will follow.

Sometimes we need to see when the rate of cooling is just beginning to bend. For this we look at the third derivative or even the fourth derivative for the beginning of the beginning of the acceleration that is an important thermal event.

Using derivatives it then becomes possible to locate a lot of different inflections. This in turn tells something about dendritic arm spacing, grain size, percent of phase, chemistry, inoculation, modification, and many other properties of the metal which will be reflected in the microstructure and possibly in the physical properties of the sample.

Liquidus Events

The liquidus arrest is defined as the first major arrest of solidification. This bypasses oxides, Chinese script, and other small arrests. Final ductile iron may not have a liquidus arrest if the C.E. is between 4.3 and 4.55. A list of normal events within the liquidus would include:

Start of liquidus – difficult to pinpoint due to heat transfer in from outside events.
Strongest point of liquidus used as the "Liquidus" number.
Liquidus grain size indicator – steepest slope coming out of the liquidus.
End of Liquidus – metal again assumes steady state cooling.

If recalesence (reheating) occurs during the liquidus, we can introduce several other events:

TLU – temperature of Liquidus under cooling.
TLR – temperature of liquidus recalesence.
Growth temperature – same as TLR
Secondary branching arrest
Coherency point – where the dendrites interlock and the casting begins to take on minimum strength.

Recalesence can occur in metals where there is a low level of inoculation for the liquidus phase materials. TiB is used in hypo-eutectic aluminum alloys to promote liquidus nucleation. CuP is used in hyper-eutectic aluminum, and iron oxide is the nucelant for austenite in iron. Some iron samples have shown liquidus under-cooling which could lead to errors in chemistry calculations.

A separate problem in iron TA is the use of water bearing sodium silicate as a binder for tellurium. These cups experience various degrees of boiling depending on the amount of gasses generated when the iron vaporizes the tellurium and sodium silicate and its bound water. This boiling caused an average loss of 0.01 to 0.02% C and 0.03 to 0.04% loss of silicon in some simple experiments compared to a non-boil cup. In addition, the boiling cups are more difficult to keep properly filled, and this will lead to additional variations in TA results because the thermal couple is no longer in the center of the sample mass.

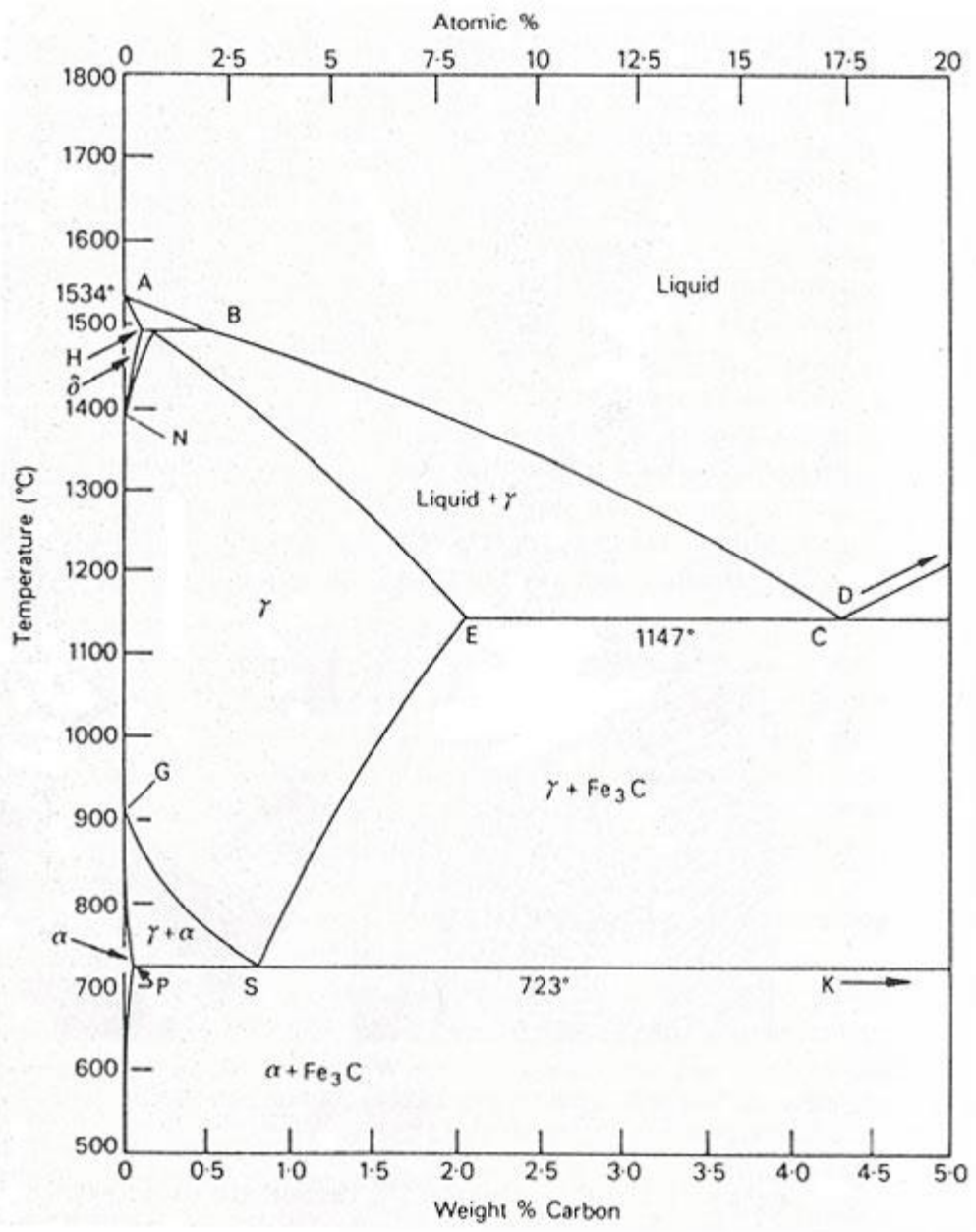
Eutectic Events

The eutectic arrest is where most of the solidification takes place, and is generally the largest and longest arrest. During the eutectic is when many micro-events can occur. Beta crystals in Aluminum often occur at the start of the eutectic, while gas bubbles generally form in the first half of the eutectic. Carbides in iron and shrinkage in most metals occur towards the end of the eutectic. These events show up as exothermic or endothermic events on the cooling curve.

Grain Boundary Events

Grain boundary events include micro-segregation, grain boundary phases such as magnesium silicide and copper in aluminum, phos arrests in high phos irons, and grain boundary stress. Micro segregation refers to the tendency of low melting phases to concentrate in the grain boundaries. A large amount of these tramp elements can suppress the end of freezing (solidus) point by as much as 50 C below that of a super clean metal.

Grain boundary stress is the area above the zero curve of the total arrest. This endothermic area is due to shrinkage stresses and disorder in the grain boundaries. Some have used the height of the EoF point as an inverse indicator of shrinkage tendency. If shrinkage did occur, the thought is that there would be less stress in the grain boundary. So the higher the grain boundary stress, the less shrinkage has occurred. This method does not take into consideration that some metal microstructures have more or less need for shrinkage to occur.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Temperature (°C)
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γ + α
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