Thermal Analysis

Given at the Ductile Iron Society Meeting 6/14/01
By W.F. Shaw & B.T. Blatzer

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With this presentation being the first part of this session on thermal analysis, we felt it would be good to review a bit of the history behind this technique or tool that has been available for routine application for over 35 years. Let me first note that, while we often use the term "cooling curves", our preferred title for this topic is thermal analysis or TA, which we'll use for the rest of our presentation.

Well before the commercial development of TA for cast irons, it was used in studying solidification of all types of materials including cast irons, and one of the earlier references to its use was in Alfred Boyle's book, "The Structure of Cast Iron", published in 1946. Examples of two figures from that book are shown in Fig. 1 and 2 (Fig. 48 & 55 from Boyles). That work and most others over the years, however, utilized platinum/platinum-rhodium thermocouples.

The development of the currently used practice of low cost, expendable thermocouples was the outgrowth of work on risering by the Gray Iron Research Institute, our previous company name, in the 1950's during which they found that chromel/alumel rather than platinum/platinum-rhodium thermocouples could be used. The temperatures involved were actually above those typically recommended for chromel/alumel but this material was reliable due to the short exposure times. This work led to a rapid test for carbon equivalent based on the good correlation between carbon equivalent and liquidus temperature as shown in Fig. 3 and 4.

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Some similar work was underway at BCIRA about the same time, however they were still using platinum platinum-rhodium thermocouples & a somewhat larger sample mold.

Figure 1 - Cooling curve of Melt No. 4

Figure 2 - Cooling curves of castings made from Iron No. 133. Curves on left from castings poured 2 minutes after inoculation. Curves on right from castings poured 32 minutes after inoculation.
Figure 3 - Relationship is shown between liquidus and eutectic thermal arrest temperatures and carbon equivalent determined by chemical analysis.

Figure 4 - Relationship of carbon equivalent data determined by cooling curve method and by chemical analysis.

The initial GIRI work involved oil sand cores with expendable thermocouple assemblies inserted as shown in Fig. 5 and 6. By 1962 there were 10 GIRI member foundries using this tool in production for measurement and control of carbon equivalent, obtaining CE values in less than a minute. The literature includes a number of articles on this topic by Dan Krause and Fred Kasch of GIRI. GIRI brought Leeds & Northrop into this work in the early 1960’s which resulted in the development of relatively low cost shell mold expendable cups that evolved into the various types in use today. By the late 60’s to early 70’s there were about five TA cup manufacturers.

Figure 5 - Carbon equivalent - Cooling curve specimen - Core box detail.
Then in the early 1970's Alan Moore at BCIRA carried out further work that led to the fairly reliable calculation of carbon from TA curves utilizing the addition of tellurium to the cups. The tellurium caused the iron to solidify as white iron, providing a white iron eutectic temperature, which, combined with the liquidus temperature of the iron, allowed for rapid carbon calculation and even an estimated silicon analysis. This provided another highly useful tool for melting that almost all of you probably use today.

This also led, however, to some initial problems regarding reliability of this method. When L&N produced the first BCIRA Carbon Calculator (Fig. 7), it provided carbon values in North American foundries approximately 0.04% lower than combustion carbons from the same sample. This difference was confirmed during a joint visit to a number of our member plants by Dan Krause of GIRL and some BCIRA and Leeds & Northrop staff. They determined that the reason for this difference was due to the fact that the work by GIRI and other groups was based on the 1948 IPTS while the new BCIRA work utilized the new 1968 IPTS. This quickly resulted in production of a new carbon calculator for U.S. foundries as shown in Fig. 8. As far as I know, this potential problem was seldom, if ever, noted in the literature except in our reports, although today the option of 1948, 1968 or the newer 1990 IPTS scale is available on some TA units.

Although this problem was resolved, the different IPTS temperature scales continued to cause some problems since the U.S. iron and steel industry primarily retained the 1948 scale while most other countries have since converted to the 1968 or even the newer 1990 IPTS. In our temperature range, however, there are extremely small differences between the 1968 and 1990 scales.
We present this information today primarily to inform about this problem since it partly explains some of the differences in the equations, charts and graphs generated by various researchers as shown in Fig. 9. But foundry men should at least be aware of related problems when studying the literature or when checking instrument calibrations in your plants. Any such differences are minor in an application such as immersion temperature measurement but can be major in a thermal analysis application. An example of possible errors resulting from mixing the different IPTS scales is shown in Fig. 10.

![Figure 9](https://www.ductile.org/magazine/2002_1/thermal.htm)

**Temperature Variations From Differences in IPTS Calibration Between Type S Thermocouple and Instrument**

<table>
<thead>
<tr>
<th>Instrument Calibration</th>
<th>1948</th>
<th>1968</th>
<th>1948</th>
<th>1968</th>
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<tbody>
<tr>
<td>Thermocouple Calibration</td>
<td>1948</td>
<td>1968</td>
<td>1948</td>
<td>1968</td>
</tr>
<tr>
<td>2500°F</td>
<td>2500</td>
<td>2503.4</td>
<td>2496.0</td>
<td>2507.5</td>
</tr>
</tbody>
</table>

![Figure 10](https://www.ductile.org/magazine/2002_1/thermal.htm)

One other problem that arose after the BCIRA Carbon Calculator was that of insufficient tellurium in some of the TA samples caused by a number of variables. It was particularly evident in higher C.E. irons that are more difficult to chill and resulted in inaccurate white iron eutectic temperatures and thus errors in carbon analysis and even CE analyses, in some cases, since tellurium does increase liquidus temperatures by up to about 61°F. We spent quite a bit of time in the 1970's and even the 1980's working with our member plants and cup suppliers on resolving this problem. One unique problem we ran into was a batch of cup receptacles in which both pins were the same alloy, either chromel or alumel. Once we figured out what it was, we immediately notified our plants and the supplier to make sure that they were replaced.

With the foregoing as background, let's briefly review some of the past work on TA applications for ductile iron, although we can only touch on a few examples. Our primary reasons for doing this are to, first of all, remind the younger industry personnel that there has been considerable research in the past and second, hopefully, to make all of you more receptive to continuing developments in this area. And perhaps third, we hope that some of you will be involved in the work that will further the application of this technique in production foundries. Research work on TA is interesting and helpful, but the real value is in its practical application.

You'll hear more about the ATAS system later in this talk and in the next two presentations. But for those of you who can't currently justify the cost of such a system, the following few examples from the literature and Bruce's information might stimulate you to use your current TA system to improve your metallurgical control. We are, by the way, speaking here about metallurgical "fingerprinting" as I've called it for many years via use of non-tellurium TA cups, not the conventional use of TA for chemical analysis measurement and control.

Two statements, however, are extremely important regarding plant applications. First, the use of TA methods for metallurgical control will not likely be of much help unless you first have good chemistry and temperature control of your iron. And second, there are a number of potential errors in TA sampling and measurement that need to be eliminated or at least minimized in order to effectively utilize this
technique, some of them highlighted in my earlier comments.

Let me preface our further comments by stating that ductile iron TA curves, except for base irons, are much more complex than those for gray iron, with considerable variation in their behavior both above and through the graphite eutectic region.

Note also that it's especially important when reviewing TA work by various authors to remember that each of them may have used different makes and sizes of TA cups as well as IPTS calibrations that would affect their results to some extent. For example, work by Gary Strong in the early 1980's used the smaller (Mark III) TA cups with vertical thermocouples while Heine's earlier work used the larger TA cups with vertical thermocouples while later work utilized the larger cups with horizontal thermocouples. Heine, Bradley et al also published some work in 1989 comparing the various types and sizes of TA cups and their relative cooling rates and other features.

Some fairly early work on Ductile Iron was reported on by Heine, Loper & Chaudhari in the 1974 AFS Transactions; they did TA work first on laboratory heats and then on commercial irons. Fig. 11 through 13 present some TA definitions from that work plus a series of final ductile iron TA curve of commercial irons at two different manganese levels.

<table>
<thead>
<tr>
<th>Key to Symbols used</th>
<th>Thus:</th>
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<tr>
<td>T</td>
<td>TAL denotes the temperature at which primary austenite forms in hypoeutectic iron melts.</td>
</tr>
<tr>
<td>A</td>
<td>TGL Denotes the temperature at which primary graphite forms in hyper-eutectic iron melts.</td>
</tr>
<tr>
<td>L</td>
<td>TEN Denotes the temperature at which initial nucleation and limited growth of eutectic occurs. (This arrest is absent on curves 1 and 2)</td>
</tr>
<tr>
<td>E</td>
<td>TEU denotes the lowest temperature to which iron melts undercool prior to beginning of bulk, eutectic growth.</td>
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<tr>
<td>N</td>
<td>TER denotes the maximum temperature on eutectic arrest, which results from recalescence due to latent heat of solidification of eutectic phases. Often TER = TEU as shown by curve 3 above.</td>
</tr>
<tr>
<td>U</td>
<td>TS denotes the solidus temperature for the alloy (Generally difficult to identify on eutectometer cooling curves)</td>
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By definition:

\[(\text{TEN} - \text{TEU}) = \text{Eutectic undercooling}\]
\[(\text{TER} - \text{TEU}) = \text{Eutectic recalescence}\]

Figure 11 - Typical eutectometer cooling curves illustrating the nomenclature used in text.

Figure 12 - Cooling curves for MgFeSi treated and post inoculated commercial irons. Mold: (plain) eutectometer. Ferritic grades (Mn ~ 0.35).
A summary of just a few of their observations from that work is as follows:

1. Curves from good ductile iron typically exhibit relatively flat eutectic arrests followed by a rather steep tail end.

2. Nodularity generally increases with the amount of undercooling up to a point beyond which carbides tend to occur.

3. If TEU drops below 2075°F or TER below 2085°F, carbides and/or intercellular graphite occur, although carbides may be minimized in cases of high silicon contents.

4. TER for good ductile iron is typically about 40° - 50°F less than the calculated equilibrium eutectic temperature, TE.
   (This suggests an optimum TER of ~2094°F +/- 5°F @ 2.50% Si.)
   \[ TE, °F = 2117 + (11.7 \times \%Si) \]

5. Eutectic recalescence, TER - TEU, of over 15°F is a clear sign of occurrence of vermicular, flake or irregular compacted graphite.

6. Nodule count increases with amount of eutectic recalescence, (or probably the nodule count determines the degrees of recalescence), but only up to a point beyond which non-spheroidal graphite occurs.

7. A high rate of recalescence between TEU and TER suggests high nodularity and nodule count. A slow rate may indicate presence of carbides.

8. Rapid cooling from 2050°F on the curve is a sign that carbides are unlikely to be present. A cooling rate of about 20°F/minute is typical of a carbide-free iron.

In the 1983 AFS Transactions, Gary Strong, a former student of Prof. Heine's, presented some practical applications of the earlier work by Heine and some of these are shown in Fig. 14 - 16.

Figure 13 - Cooling curves for MgFeSi treated and post inoculated commercial irons. Mold: (plain) eutectometer. Pearlitic grades (Mn ~0.65)

Figure 14 - Initial iron poured vs. last iron five minutes later.
Figure 15 - Standard treated iron vs. bismuth and bismuth and sprue inoculation.

Figure 16 - Effect of increasing cerium in MG treatment on inoculated iron cooling curve.

A presentation by W. Knothe at the 1987 BCIRA International Conference put forth some interesting data and methods for process control and are summarized in Fig. 17-23. These curves represent a shop using the Fischer process for ductile iron production. Of special interest to me was the fact that the author included statistical information with his TA curves, showing means and standard deviations for the various features of the curves. I’m unaware of any other papers providing such information.

Figure 17 - TA Curves at each stage of a Fischer process Ductile Iron
Figure 18 - Cooling curve of a composition adjusted base iron.

Figure 19 - Cooling curve prior to magnesium treatment in the Fischer converter.

Figure 20 - Cooling-curve for an uninoculated magnesium-treated melt.
A few years later, Heine and Bradley carried out further work at the U. of Wisconsin relating shrinkage to TA curve behavior on both lab and commercial irons. One of the early results of this work, comparing three production foundries, clearly confirmed that higher levels of manganese, chromium and magnesium promote low TEU temperatures, which in turn lead to increased shrinkage tendency. This led to subsequent changes in chemical analyses and process controls at the foundries which significantly reduced shrinkage related scrap. Other TA work by Hummer in Austria provided confirmation of some of these effects. And work by both Heine and Hummer pointed out the effects of oxidation on TA curves, although Breeden of BCIRA refuted Heine's claims about oxidation in a 1982 report.

There are numerous other authors and papers we could refer to, but we hope that these few example of past work and Bruce's information will stimulate your thinking as to the potential benefits of TA process control. It's not a panacea for all of our problems, but it is a tool that, if wisely used, can be extremely useful.

Working in an industry where change is one of the few constants and quality demands are rapidly increasing, can we afford not to use all of the potential process control tools available to us? We can be sure that all or some of the following will change from time to time: charge materials such as steel, pig iron, coke and carbon raisers; ferroalloys, including inoculants, since they are produced with varying...
charge materials; and nodulizing and inoculating methods. All of these potentially affect our ductile iron process and the resultant metallurgy and consistency of our iron.

With the foregoing as background, Bruce Blatzer will now summarize some of the TA work on Ductile Iron that we've been doing with our member companies, although recently we've been doing more with Gray Irons. It's far from complete or exhaustive, but we feel that we need to continue encouraging our members and our industry to use every tool available to improve the consistency of our iron and castings.