

Use of thermal analysis in the iron foundry: BASIC PRINCIPLES

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AZTERLAN Metallurgy Research Centre (www.azterlan.es) will break down, through a series of three articles, the basic principles of thermal analysis, a widely used technique for the control of the casting process.

In this first article, fundamental operating principles of the technique are presented. In a second article the main applications successfully implemented in highly competitive foundries will be developed. Finally, a third article will share a more advanced perspective on the online control of the quality of manufactured parts achieved by coupling thermal analysis technology with simulation process of filling and feeding systems.

INTRODUCTION TO THERMAL ANALYSIS

The solidification process of a metal and its subsequent cooling to ambient temperature give rise to thermal transformations associated with the nucleation and growth of the different phases present during solidification. These transformations have a direct effect on the cooling curve.

Thermal analysis represents, in the shape of a curve, the evolution of the temperature of the metal with respect to the elapsed time and is a very valuable tool for studying metal behaviour: the nucleation of graphite and its subsequent growth, the formation of carbides or reverse tempering, the transformation of austenite (γ) into a fully ferritic or pearlitic matrix, among others.

This curve, which shows the cooling evolution, is typically obtained by measuring the temperature of the metal in a sand cup containing a thermocouple at the thermal centre (fig.1).

Thermal analysis provides valuable information that can be used to monitor and improve both the quality and performance of the casting process and cast products.

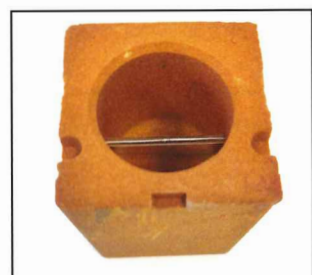


Fig.1 Example of a sand cup used to record cooling curves



Fig.2 Main screen of a thermal analyser (in this case, Thermolan® system), showing the relevant parameters obtained from this analysis

With the aim of developing useful tools to enhance foundry competitiveness, AZTERLAN has developed the thermal analysis tool Thermolan®.

BASIC PRINCIPLES OF THERMAL ANALYSIS FOR CAST IRON

The analysis of the behaviour of the metal during the solidification process is analysed considering the two most relevant processes: the liquid-solid transformation and the solid-solid transformation. In both cases, events occur that affect the cooling curve and are reflected in the thermal analysis of that curve.

Liquid-solid transformation

The thermal analysis of cast iron is based on the Fe-C phase diagram, which, despite being theoretical, helps understand the fundamentals of thermal analysis.

Cast iron is defined as an iron based alloy with a carbon percentage between 2.06 per cent and 6.67 per cent (the percentage corresponding to the carbon content dissolved in cementite). Steels, on the other hand, have a carbon content of less than 2.06 per cent (fig.3).

However, there are two solidification systems for cast irons, the stable system and the metastable system.

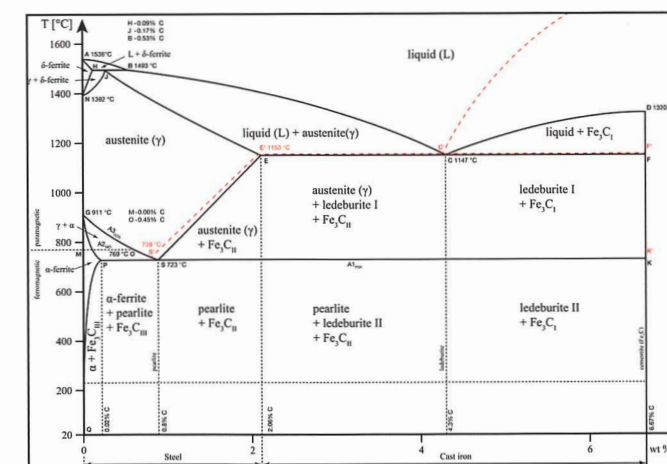


Fig.3 Fe-C phase diagram. (source: Wikimedia Commons) https://commons.wikimedia.org/wiki/File:Iron_carbon_phase_diagram.svg

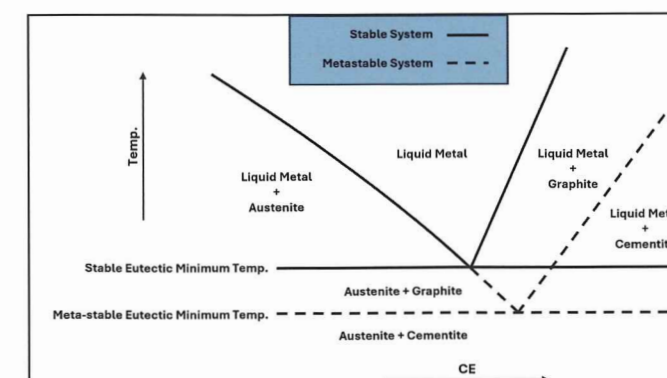


Fig.4 Eutectic region of the Fe-C diagram, showing the eutectic temperatures of the stable and metastable systems

The difference between the two lies in the fact that in the stable system the carbon present in the alloy precipitates as a phase called graphite. Graphite can appear in the form of spheroids, vermicles or flakes depending on the Mg-S ratio of the alloy. In the metastable system, all the carbon precipitates forming iron carbides (Fe_3C). Compared with carbide irons, graphitic cast irons exhibit higher ductility and strength and lower hardness, providing very attractive mechanical properties for a wide range of applications.

From the perspective of thermal analysis, these two systems clearly differ during the liquid-solid transformation (eutectic temperature) (fig.4).

Iron carbides require slightly lower transformation temperatures (1147°C), whereas graphite precipitates at higher temperatures (1153°C).

The theoretical eutectic temperatures shown in the Fe-C diagram differ from those recorded in practice, where the gap between both temperatures increases by the effect of silicon present in standard iron alloys (fig.5).

In cast iron the carbon axis of the Fe-C diagram is replaced by another relevant concept that evaluates the effect of certain alloying elements (mainly Si and, to a lesser extent, P) on the displacement of the eutectic position. This concept is known as carbon equivalent (CE).

In simplified terms, the CE of an alloy is calculated as follows (equation 1):

$$\%C_{\text{equivalent}} = \%C + \frac{\%Si}{3} + \frac{\%P}{3} \quad \text{Equation 1}$$

The difference in eutectic temperature in the two solidification systems provides the first indication for distinguishing between a graphitic casting and a carbidic casting.

Additionally, based on the Fe-C phase diagram (fig.3) and equation 1, it can be observed that the shape of solidification curves recorded by thermal analysis systems is directly related to the CE content.

Accordingly, depending on CE value, cast iron can be classified as eutectic, hypoeutectic or hypereutectic.

The eutectic composition is an alloy with CE equal to 4.30 per cent. In this alloy, both austenite (phase γ) and iron carbides (or graphites in the stable system) precipitate simultaneously once eutectic temperature has been reached.

In hypoeutectic compositions ($\text{CE} < 4.30$ per cent), austenite (γ phase) precipitates when the cooling temperature reaches the temperature of liquidus. As the austenite precipitates, the remaining liquid is enriched in carbon (CE) until it reaches the eutectic composition, at which point the remaining liquid precipitates jointly as γ and iron carbides (or graphite).

Finally, in hypereutectic compositions ($\text{CE} > 4.30$ per cent), iron carbides (graphite) initially precipitate at the liquidus temperature; and, at eutectic temperature, austenite and carbides precipitate simultaneously.

Any precipitation happening during solidification and subsequent cooling presents a change in behaviour of the cooling curve, making both the liquidus and eutectic temperatures easily identifiable (fig.6).

In the eutectic zone, undercooling occurs due to thermodynamic inertia of the metal. This undercooling gives rise to a minimum eutectic temperature, followed by recalescence, caused by the exothermic nature of graphitic precipitation, describing a characteristic point known as maximum eutectic temperature.

Finally, by analysing the derivatives of the curves, the solidus temperature, at which the entire alloy has solidified, is determined.

Following the logic shown in the Fe-C phase diagram, it can be concluded that for hypoeutectic compositions, the lower the liquidus temperature, the higher the CE of the cast iron, at least up to the eutectic composition ($\text{CE} = 4.30$ per cent).

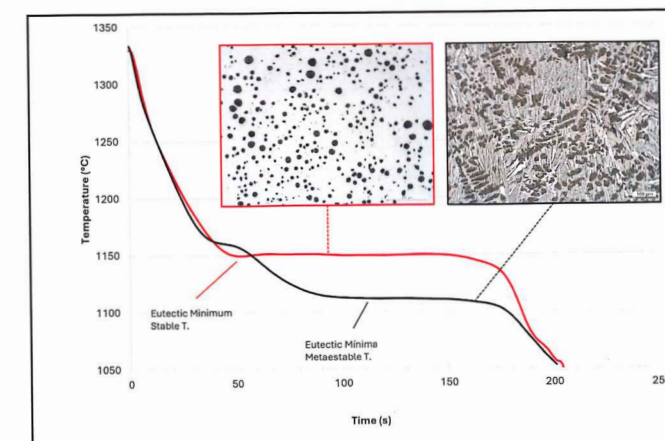


Fig.5 Example of cooling curves for the stable (red) and metastable (black) systems with a silicon content of 2.18 per cent

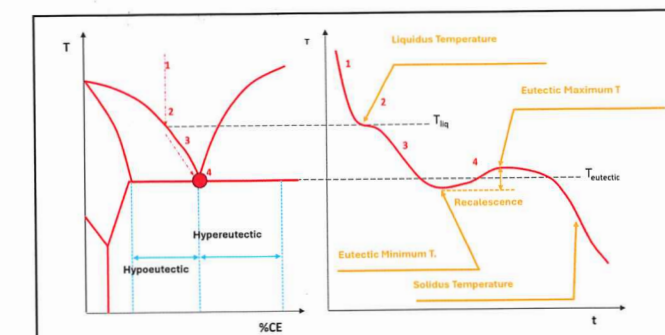


Fig.6 Representation of a solidification curve in relation to the Fe-C diagram

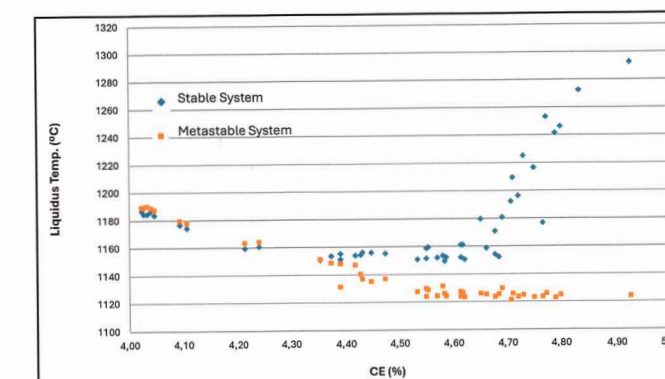


Fig.7 Representation of the temperature of liquidus against the CE, for both stable and metastable systems analysed with Thermolan®

In hypereutectic compositions, in theory, the temperature of the liquidus and the CE will be directly proportional.

However, we speak of 'theory' because, from the theoretical diagram to the experimental practice, some important differences can be observed:

- Following the cooling of a metastable system, in practice, no slight stop in solidification associated to the temperature of the liquidus is observed.
- Additionally, for a stable system, it is observed that the so-called eutectic point actually corresponds to a CE range between 4.30 and 4.60 per cent.

These two events have been reported experimentally and are shown in fig.7, which plots liquidus temperatures for two metals cooled following both systems (stable and metastable).

Apparently, following what the Fe-C phase diagram describes, one might assume that the minimum eutectic temperatures are fixed for the stable and metastable system. But, in reality, there are various chemical elements that interfere with this temperature. Fig.8 illustrates the effect of certain elements, such as Si, Ni, Cu, Co, Al, Sr, Mn, P, Sn, Mo, Sb, Cr, V, Ti and Te on the minimum temperature in both systems.

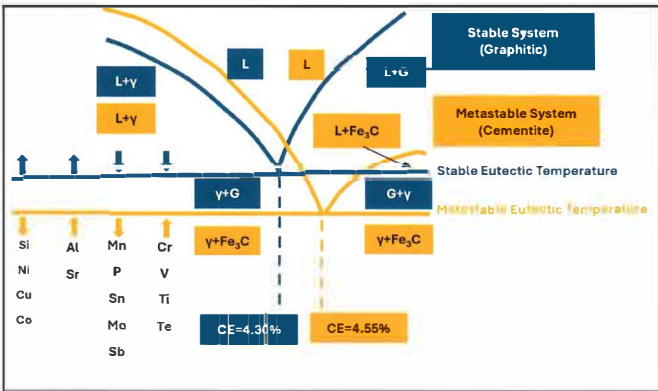


Fig.8 Effect of various chemical elements on minimum eutectic temperature in the stable and metastable systems

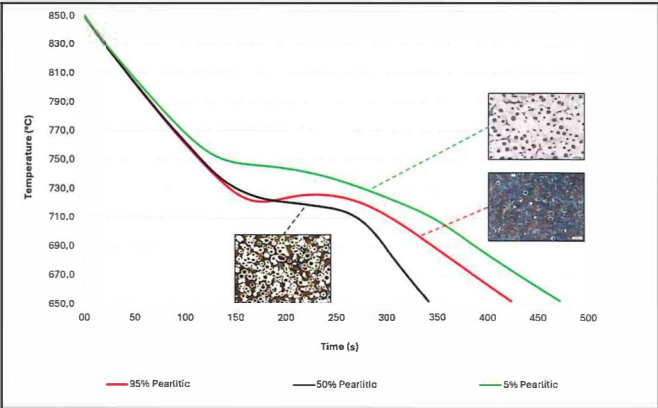


Fig.9 Cooling curves of fully pearlitic, fully ferritic and mixed-matrix nodular cast irons

Among all elements, silicon has the greatest influence on the minimum eutectic temperature. Hence, the value of the minimum eutectic temperature makes it possible to calculate the silicon content of cast iron.

$Si = f(\text{min metast. } T_{eut})$ Equation 2

This equation is applicable only to metals cooled under the metastable system, as the precipitation of iron carbides does not generate recalcrescence and the curve is not affected by any other factors.

On the other hand, and as mentioned earlier, the liquidus temperature is directly related to the CE content of the metal. Therefore, starting from equations 1 and 2, the following relationships can be derived:

$$CE = C + \frac{Si}{3} + \frac{P}{3} = C + \frac{f(\text{min metast. } T_{eut})}{3} + \frac{P}{3} = f(T_{liquidus})$$
$$C = f(T_{liquidus}) - \frac{f(\text{min metast. } T_{eut})}{3} - \frac{P}{3}$$

Equation 3

Equation 3 allows calculation of the carbon content from the recorded curve and is applicable only when the CE is hypoeutectic in the metastable system ($CE < 4.55$ per cent). For higher CE values, this formula is not applicable because the shape of the curve no longer varies, providing similar minimum eutectic and liquidus temperatures, and consequently similar carbon and silicon contents. For these higher CE values, AZTERLAN has developed and validated a system that combines a stable and a metastable curve to perform this calculation.

Solid-solid transformation

As is well known, once the metal has solidified, austenite (also, γ iron) undergoes atomic rearrangement into a solid state. This occurs because austenite is not stable at room temperature, and undergoes transformation at temperatures below 725°C.

In standard nodular, vermicular and lamellar cast irons, austenite is transformed into ferrite and/or pearlite (in usual cooling processes). This transformation happens in the eutectoid region, and similarly to what occurs in eutectic zone, the cooling curve undergoes shape changes depending on the type of transformation undergone by γ iron (fig.9).

This eutectoid transformation depends on cooling rate as well as on the alloying elements dissolved in the metal. In this way, the more Cu, Mn, Sn and Cr (among others) dissolved in it, the more pearlitic the metal matrix is promoted. On the other hand, the alloys rich in Si, Ti, Al and Zn, promote a ferritic matrix.

Therefore, it can be deduced that thermal analysis enables prediction of the final metallic matrix state at the end of the cooling process.

POTENTIAL OF THERMAL ANALYSIS SYSTEMS

These theoretical fundamentals of thermal analysis systems highlight their potential for optimising foundry production processes, demonstrating how understanding is transformed into process control and subsequently into tangible, implementable actions.

With this approach, the next article in this series will address the practical use of thermal analysis in foundries, focusing on increasing metal control during the casting process to improve metallurgical quality and ultimately produce sound castings.

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Technical papers are required to be in a Microsoft Word format with any supporting imagery supplied as separate, high resolution jpeg files. Submissions should be sent to the editor at: lynn@foundrytradejournal.com