Finding the True Eutectic Point – An essential task for efficient process control of Ductile Iron

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ABSTRACT

The position of the eutectic point is traditionally considered to correspond to a carbon equivalent of 4.3% for normal cast iron alloys. The paper describes that the eutectic point is not just a function of the chemical composition but it is also a function of the nucleation level for graphite as well as the cooling rate. The eutectic point can therefore vary considerably e.g. from 4.1 to 4.6% although the chemical composition is identical. This can lead to errors in controlling the metallurgical process especially for ductile iron. The author suggests a new definition of the eutectic point based on thermal analysis.

INTRODUCTION

The traditional iron-carbon binary phase diagram shows the eutectic point at 4.3% carbon for a melt solidifying with precipitation of austenite and carbon as graphite but without primary austenite or primary graphite. The binary Fe-C eutectic temperature is 1148°C (2098°F). The diagram, although only intended for the binary Fe-C alloy, is often used for industrial alloys such as cast iron that also contain silicon, phosphorus, manganese, sulphur, chromium, nickel, molybdenum etc. Of these elements, silicon and phosphorus have a significant effect on the liquidus temperature. For example, silicon and phosphorus push the eutectic point to the left*, i.e.* they reduce the carbon content of the eutectic point. The effect of silicon on the liquidus temperature has been found to be equivalent to about 25% of the effect of carbon. The effect of phosphorus is about 50%. This means that an increase in 1% silicon is equivalent to an increase in 0.25% C and that an increase of 0.06% P is equivalent to an increase of 0.03% C. Knowing the exact position of the eutectic point is important both for grey and ductile iron in order to control the solidification and, hence, for avoiding casting defects.

CONCEPT OF CARBON EQUIVALENT (CE)

Plain cast iron is an alloy of carbon and silicon. The phase diagram for such a ternary Fe-C-Si alloy is complex. Phase diagram representation becomes even more complex when phosphorous and other elements are present. For this reason, a simplified and convenient

Carbon Equivalent (CE) formula is defined and commonly used in the industry. The method estimates a number, equivalent to the effect of carbon for each of these elements. Temperature as a function of CE is traditionally represented by a binary phase diagram as shown in **Figure 1**.

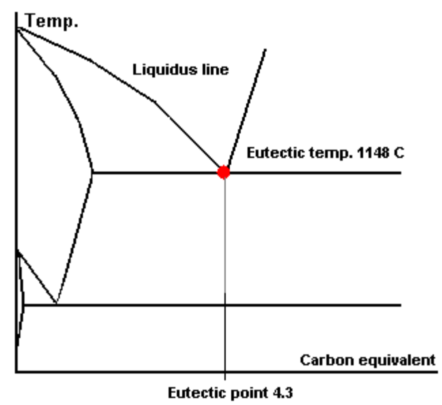


Figure 1 : Binary phase diagram

Numerous studies have been made on the relationship between CE and the liquidus temperature. The relationship is found to be almost linear. The most correct formula for CE is CE= C+Si/4+P/2. Thus, an iron with 3.65% C, 2.4% Si and 0.1% P (CE=4.3), would be considered to solidify fully eutectic i.e. without any precipitation of neither primary austenite nor primary graphite.

PROBLEM WITH SIMPLIFIED DEFINITION OF CE AND THE EUTECTIC POINT

The described, traditional, concept is widely accepted but seems to be too simplified. It has been shown that CE calculated from chemical analysis does not always agree with the one obtained from liquidus relationship. This is because of the influence of other elements on liquidus. Using CE calculated from the chemical composition and assuming that the eutectic point is at 4.3% as basis for grey and ductile iron process control can be misleading and can lead to costly mistakes.

One must be aware of the fact that the iron-carbon diagram is a diagram constructed at equilibrium conditions and without any other alloying elements. In reality, many elements influence the liquidus temperature, e.g. C, Si, P but also several other elements such as Al, Mg, Mn, Ni, O that are not even included in the traditional CE-formula. The liquidus temperature integrates the effect of all of these elements in the alloy. Therefore, determining CE based on the liquidus temperature is more accurate and true than estimating CE from the chemical compositions. The author suggests naming the carbon equivalent calculated from the liquidus temperature as the "Active Carbon Equivalent Liquidus" (ACEL). The liquidus temperature should be determined using test cups without tellurium to achieve the highest accuracy.

The eutectic temperature can vary considerably even if the chemical composition is constant. The reason is that it depends not only on the chemical composition but also to a large degree on nucleation of graphite and cooling rate. It is well know that the eutectic temperature can increase up to 10°C or more if the iron is inoculated. A high cooling rate decreases the eutectic temperature and as it comes closer to the white eutectic temperature, the risk for chill increases. In the phase diagram, the eutectic point is where the liquidus line meets the horizontal eutectic line. The liquidus line is mainly dependent on the chemical composition, but the horizontal level of the eutectic line can vary so the conclusion must be:

Neither the eutectic composition nor the eutectic temperature (stable solidification) are fixed at constant values determined by the chemical composition.

A NEW DEFINITION AND METHOD FOR FINDING THE TRUE EUTECTIC POINT

One way of measuring solidification and tracing the actual eutectic composition and temperature is thermal analysis. With sophisticated electronics and refined software it is possible to record and analyse cooling curves very accurately. The ATAS instrument, developed by NovaCast has been used in this study.

The best method to evaluate if an alloy solidifies eutectic is to use cooling curve analysis with "grey" curves i.e. using test-cups without any addition of tellurium. The method and definition suggested by the author is as follows:

The True Eutectic Temperature (TEP) is the temperature where the liquidus temperature coincides with the grey eutectic temperature (TElow). Thus, the eutectic composition is not always when CE=4.3 %. The True Eutectic Point is in fact a dynamic value that depends on the chemical composition, the cooling rate and the nucleation level. The new definition can be simplified as in **Figure 2**, which shows the liquidus and the eutectic lines and the eutectic point where the lines meet.

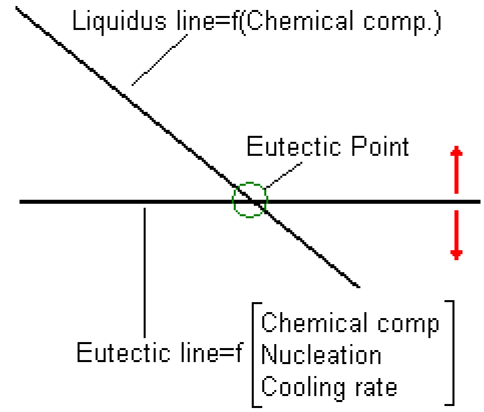


Figure 2 : New definition of true eutectic point.

A typical cooling curve for a ductile iron is shown in **Figure 3**. Note that both TL and TElow are 1145°C! It is, thus, clear that the iron has solidified fully eutectic.

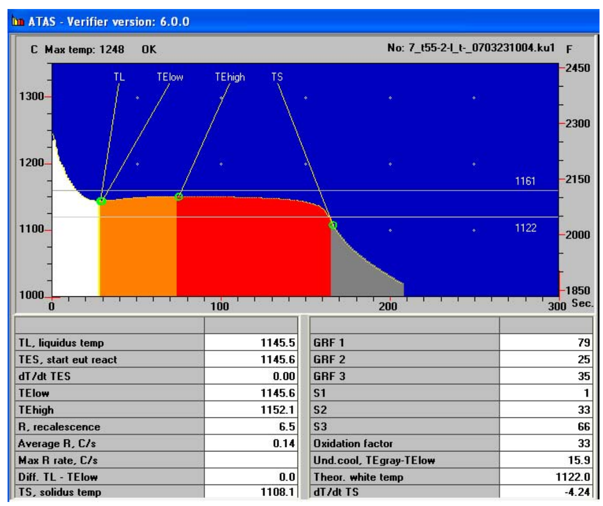


Figure 3: Typical ductile iron cooling curve

For hypo-eutectic compositions, the liquidus temperature can be used to estimate the active carbon equivalent (ACEL) using the formula ACEL=14.45 – 0.0089*TL. The low eutectic temperature (TElow) is influenced by many elements such as Si, Al, P, Mo, Cr and Cu but also to a large extent by the nucleation status of the melt and as well as the cooling rate. The nucleation and thereby TElow can easily be influenced (increased) by inoculation. In a hypo-eutectic alloy e.g. a base iron for ductile iron, an increase in TElow reduces the distance to TL and the effect is that the alloy will solidify with less primary austenite or perhaps in a eutectic way if TElow equals TL.

If we accept the suggested definition that the eutectic point is reached when TL=TElow, then we must accept that the eutectic point can vary not only as a function of TL but also as a function of TElow! The old definition of the eutectic point as when the chemical composition equals a carbon equivalent of 4.3% seems wrong!
Our experiences with cooling curve analysis of base and final ductile iron (which often have a eutectic composition) have shown that TL can be equal to TElow at different temperature levels. This is illustrated in **Figure 4** and **Figure 5**.

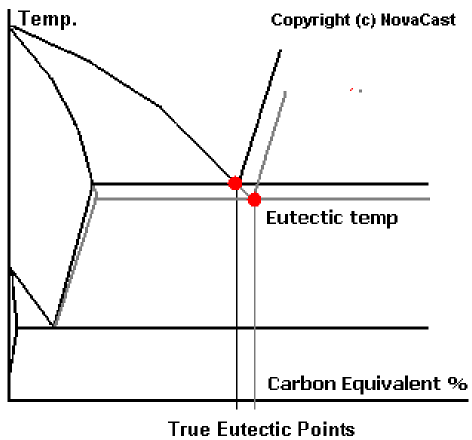


Figure 4: Principle of true eutectic points

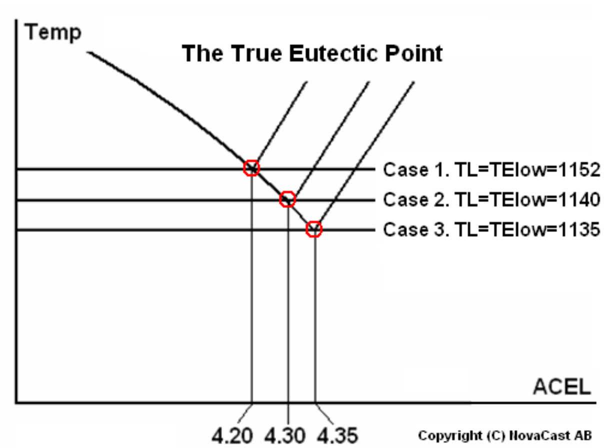


Figure 5: Examples of cases

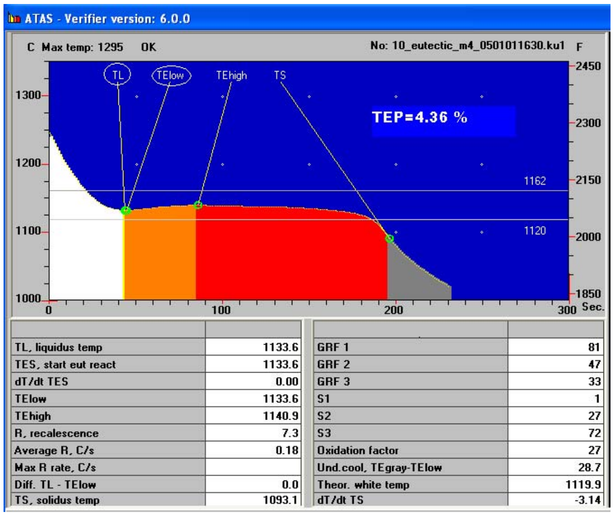
In case 1, the liquidus temperature is 1152 and ACEL can be calculated to 4.2% using the formula ACEL=14.45 – 0.089* TL. In this case, TElow is also 1152, which shows the alloy has solidified fully eutectic!
The True Eutectic Point is calculated using the formula TEP=14.45 – 0.0089*TElow. For case 1 TEP= 4.2% i.e. the same as the ACEL value.

In case 2 both the liquidus and the low eutectic temperatures are 1140°C which indicates eutectic solidification and that the True Eutectic Point in that case is 4.3%. In case 3 the True Eutectic Point is 4.35% and the alloy should solidify hypereutectic using the old definition of the eutectic point. However as the True Eutectic Point is 4.35% and ACEL is also 4.35% the alloy solidifies eutectic and without any primary graphite!
The liquidus temperature (TL) is mainly influenced by the active carbon equivalent (ACEL). The low eutectic temperature can vary considerably with basically the same chemical composition if the nucleation or the cooling rate is varied. If the eutectic point is defined as when TL=TElow, then the eutectic point can vary as a function of chemical composition, nucleation and cooling rate.

If the cooling rate is high, then TElow is reduced due to undercooling. The alloy in case 2 has a eutectic point at 4.30 % at equilibrium conditions. If the cooling rate is high (thin walled casting), then TElow is reduced from 1140 to say 1130°C. The alloy will then solidify as a hypoeutectic alloy with precipitation of primary austenite which can cause a shrinkage problem. If the foundry metallurgist had been aware of the new definition of the eutectic point, he/she could increase TElow by improving inoculation or raising TElow by increasing silicon. For thin wall castings, it is well known that the target in ACEL can be hypereutectic (chemically!) but in spite of that, the alloy does not solidify with primary graphite due to a high cooling rate. The high cooling rate lowers TElow which has the effect that TEP increases.

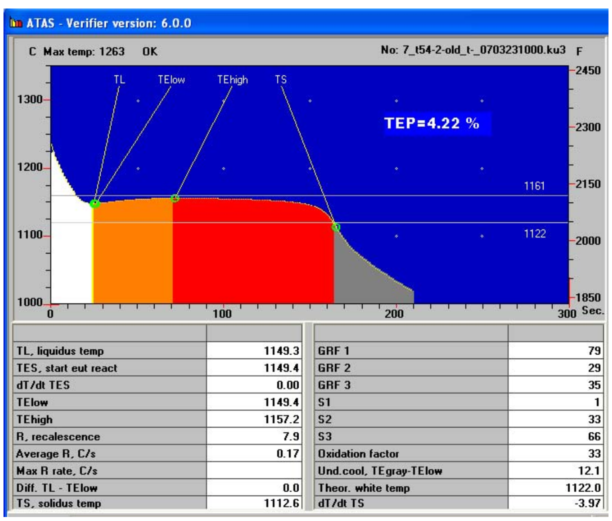
Note that the true eutectic point (TEP) can only be found if the iron is allowed to solidify without primary carbides. This means that the cooling curve analysis must be made using test-cups without any tellurium. If a tellurium cup is used, then the iron will solidify “white” and only show the white eutectic temperature which is very low (often around 1115 – 1125) and not influenced by graphite nucleation.

Figures 6 and **7** show examples of cooling curves with eutectic solidification where the true eutectic point (TEP) is 4.36% in one of the samples and 4.22 % in the other.



TL, liquidus temp	1133.6	GRF 1	81
TES, start eut react	1133.6	GRF 2	47
dT/dt TES	0.00	GRF 3	33
TElow	1133.6	S1	1
TEhigh	1140.9	S2	27
R, recalescence	7.3	S3	72
Average R, C/s	0.18	Oxidation factor	27
Max R rate, C/s		Und.cool, TEgray-TElow	28.7
Diff. TL - TElow	0.0	Theor. white temp	1119.9
TS, solidus temp	1093.1	dT/dt TS	-3.14

Figure 6: TEP is 4.36%



TL, liquidus temp	1149.3	GRF 1	79
TES, start eut react	1149.4	GRF 2	29
dT/dt TES	0.00	GRF 3	35
TElow	1149.4	S1	1
TEhigh	1157.2	S2	33
R, recalescence	7.9	S3	66
Average R, C/s	0.17	Oxidation factor	33
Max R rate, C/s		Und.cool, TEgray-TElow	12.1
Diff. TL - TElow	0.0	Theor. white temp	1122.0
TS, solidus temp	1112.6	dT/dt TS	-3.97

Figure 7: TEP is 4.22%

PRACTICAL IMPLICATIONS

It is good practice to pour ductile iron castings with alloys that are close to the eutectic point. The traditional process control method is to calculate the CE-value based on spectrometer data and to correct it so that 4.3% is reached. This method can lead to considerable variations, especially in casting properties as the CE-value calculated from chemical composition has a limited accuracy of about +/- 0.05% and because the true eutectic point is influenced by nucleation and the cooling rate. Estimating ACEL from a cooling curve improves the accuracy to about +/- 0.01%, thus, about 5 times more accurate than from a value calculated using spectrometer data.

Controlling the grey eutectic temperature within narrow limits is the key to keeping TElow and thus TEP at a constant level. By using the described concept, it is possible to reach the optimal ACEL target in relation to the true eutectic point (TEP) with high precision. The result is an iron that is more consistent and less prone to e.g. shrinkages, which will make it possible to increase casting yield. A preliminary correlation between the true eutectic points measured as ACEL as a function of the liquidus temperature when TL equals TElow is shown in **Figure 8**.

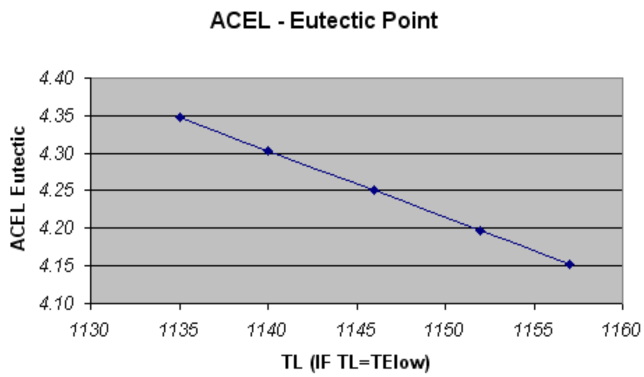


Figure 8: Preliminary correlation

In order to obtain a truly eutectic solidification on a repetitive basis, it is very important not only to keep the liquidus temperature but also the grey eutectic temperature at constant levels. As the eutectic temperature is influenced by nucleation of graphite, a good quality inoculant must be used and the amount should be dynamically adjusted based on thermal analysis measurements. The effect of inoculation is normally that TElow increases. If the alloy is hypoeutectic, it means that the distance between TL and TElow is reduced. Thereby the alloy comes closer to the eutectic point even though the chemical composition is almost the same!

The position of the "true eutectic point" is also important for grey iron. The amount of primary austenite is important both for physical and casting properties. It is a function of the active carbon equivalent (ACEL) and the true eutectic point (TEP). In order to obtain a constant amount of primary austenite, it is, therefore, important not only to keep ACEL at a constant level but also to maintain the eutectic temperature at a constant level. Additionally, for grey iron, it is very important to keep not only the liquidus temperature but also the grey eutectic temperature on a constant level using the dynamic inoculation method in ATAS.

REFERENCES

1. NovaCast Foundry Solutions AB – internal research
   www.novacast.se

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