Technique Incorporating Cooling & Contraction / Expansion Analysis to Illustrate Shrinkage Tendency in Cast Irons

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Abstract. With the more widespread adoption of thermal analysis testing, thermal analysis data have become an indicator of cast iron quality. The cooling curve and its first derivative display patterns that can be used to predict the characteristics of a cast iron. An experimental device was developed with a technique to simultaneously evaluate cooling curves and expansion or contraction of cast metals during solidification. Its application is illustrated with results on shrinkage tendency of ductile iron treated with FeSiMgRECa master alloy and inoculated with FeSi based alloys, as affected by mould rigidity (green sand and resin sand moulds). Undercooling at the end of solidification relative to the metastable (carbidic) equilibrium temperature and the expansion within the solidification sequence appear to have a strong influence on the susceptibility to macro- and micro-shrinkage in ductile iron castings. Green sand moulds, as less rigid moulds, encourage the formation of contraction defects, not only because of high initial expansion values, but also because of a higher cooling rate during solidification, and consequently, increased undercooling below the metastable equilibrium temperature up to the end of solidification.

1. Introduction

Nodular [spheroidal] graphite cast iron [Ductile iron] is a ferrous material, subjected to casting process, typically including [wt.%] 3.4 – 3.8 C, 1.8 – 2.8 Si, 0.1 – 0.6 Mn, < 0.05 P, < 0.02 S, 0.03 – 0.06 Mg, with or without rare earth elements [RE] contribution, with nodular [spheroidal] graphite precipitated during solidification. Without spheroidising treatment application [Mg or/and RE], lamellar [flake] graphite morphologies will result. Including nodular graphite particles, at higher compactness degree and consequently at reduced cutting effect of stress concentration in the metal matrix, the mechanical properties of ductile iron are significantly superior to compact graphite cast irons and especially to grey [lamellar graphite] cast irons. Despite of the eutectic – hypereutectic composition, spheroidising treatment applied to prior solidification leads to a higher solidification undercooling, favouring free carbides formation. Due to the peculiar solidification pattern of ductile iron, it is much easier for intercellular cavities to form, comparing to grey cast iron solidification. Consequently, macro and micro shrinkage will usually characterize ductile iron castings. According to Z. Jiyang [1] these contraction defects (figure 1) occur first of all because solidification will be in “mush” mode and the resulted weak solidified shell cannot withstand the expansion which occurs during eutectic freezing, due to graphite precipitation; the casting expands outwards but does not compact inwards, thus cannot form self-feeding. On the other hand, a strong segregation of carbides-
promoting elements in the eutectic inter-cells regions is typical for ductile iron solidification, favouring micro-shrinkage formation in these regions.

![Shrinkage porosity in ductile iron casting: a) micro-shrinkage, in inter eutectic cells regions; b) macro-shrinkage.](image)

**Figure 1.** Shrinkage porosity in ductile iron casting: a) micro-shrinkage, in inter eutectic cells regions; b) macro-shrinkage.

As the most important factors influencing the contraction defects [shrinkage and micro-shrinkage] formation, mould and metal variable act by different ways, such as mould deformation and enlargement tendency, volume-to-surface area ratio (cooling modulus) of casting, chemical composition of cast iron [especially expressed by carbon equivalent], graphite phase [nodularity, nodule count, size distribution], carbides [amount and distribution] and eutectic cells [size, count, distribution] characteristics, pouring temperature, metallurgical treatments [spheroidising and inoculation], difference as expansion in the surface region than in the inner region of a casting due to temperature differences [2-11]. With the more widespread adoption of thermal analysis testing, thermal analysis data have become an indicator of cast iron quality. The cooling curve and its first derivative display patterns that can be used to predict the characteristics of a cast iron. On the other hand, different techniques were developed to evaluate the succession of contraction and expansion stages during cast iron solidification, which are involved in macro- and micro-shrinkage formation.

The main objective of the present work was to introduce a specific experimental instrument and technique for simultaneously evaluating cooling curves and expansion or contraction of cast metals during solidification. Previous papers [12-14] presented information on the development of such specific equipment and a technique. Some recently obtained data are now added, to identify the most representative parameters on the cooling/contraction/expansion curves which are connected with contraction defects formation, focused on mould rigidity influence in inoculated ductile cast irons.

2. Materials and methods
Figure 2 illustrates the recorded equipment, using specialized software created in a LABVIEW program, which is able to simultaneously display both cooling and contraction / expansion curves and their respective source data. The equipment stand includes two parallel moulds (sample size 200 mm and 30 mm square cross section bar, at 0.72 cm cooling modulus –CM, and 1250 g weight). A high speed type AT-MIO10 interface records simultaneous temperature and linear displacement data. The program was capable of 5,000 readings/s and a display rate of 10 samples/s, with each sample represented by an average of 500 readings. The assembly for linear displacement measurement was checked, and an opto-mechanical transducer having a precision of 0.001 mm was used. The thermal analysis system was calibrated by a commercial (Chekmate III/Quik-Cup) instrument, which claims a resolution of 0.1°C according to IEC584/IPTS68, for K type thermocouples.

The calibration instrument accuracy is ± 0.05% + 1°C. The accuracy of the thermal analysis system was evaluated taking into account the full measurements chain from the cup (typical error: 0...+2°C, the compensation wire (error ±1°C), the contact block (error ±1°C) and the hardware (error ±1°C). As
a combined result for these chain components, the calculated error was 2.65°C, without calibration. After calibration it was reduced to less than 1°C.

Figure 2. Arrangement of twin mould cooling and contraction / expansion curves analyser (CCCA) and representative components.

A base iron was melted in a graphite crucible induction furnace (10 kg, 8000 Hz), with 5-7 min superheat at 1550-1570°C. A tundish cover ladle technique was used to treat the iron at 1500-1520°C with a 2.5 wt.% addition of Mg-FeSi alloy with a 3-10 mm grain size (45.4% Si, 6.1% Mg, 0.6% RE, 0.86% Ca, 0.69% Al). Treated irons were poured at 1350-1380°C in the specially prepared moulds included in the Cooling / Contraction Curves Analyser-CCCA (figure 2). Typical Cooling and Contraction / Expansion Curves of ductile test irons and their first derivatives are shown in figure 3, including the significant parameters. To obtain consistency in iron treatments, late inoculation (inoculant addition in the pouring basin) was preferred (0.2 wt.% inoculant, 0.2-0.7 mm grain size), from several other inoculation techniques tested. The CCCA equipment includes two work stations (moulds), which allow simultaneous testing of two inoculants with the same conditions. Different FeSi-based alloys were tested as inoculants. The time of mould filling was 3-4 sec, while the total time of iron processing (tapping, Mg-treatment, deslagging, sample pouring) was maintained within a 3.0-3.5 min range.

Green Sand Mould (GSM) with constant compactness (rigidity) (60-70 Dieter Hardness on the mould separation plane and 125 N/cm² as compressive strength on standard cylindrical samples) was compared to Resin (furan) Sand Mould (RSM) (about 89 Dieter Hardness and 1400 N/cm² tensile strength on standard samples).

The shrinkage tendency of these experimental ductile irons using the CCCA-test bars (30 mm square cross-section bar) was evaluated by three methods. (a) An X-Ray investigation was made in the front longitudinal plane of the samples. The negative films were scanned and then automatic image analysis was applied to both concentrated and macro-dispersed shrinkage (as absolute and relative surface areas); (b) A water displacement method was used to measure both open and closed [TM - maximum pouring temperature, °C; TAL/TGL/TL - temperature of austenitic / graphitic liquidus, °C; TSEF/TEN - temperature of the start of eutectic freezing (nucleation), °C; TEU - lowest temperature of eutectic undercooling, °C; TER - temperature of graphitic recalescence, °C; TES-temperature of the
end of solidification (end of solidus), °C; TEM - maximum recalescence rate, °C/s; Tst – stable (graphitic) eutectic equilibrium temperature, °C; Tmst – metastable (carbidic) eutectic equilibrium temperature, °C; ΔTs - range of equilibrium eutectic temperature (ΔTs = Tst - Tmst), °C; ΔTm – maximum degree of undercooling (ΔTm = Tst - TEU), °C; ΔTr - recalescence (ΔTr = TER - TEU), °C; τES - duration of eutectic solidification, sec; τts - duration of total solidification, sec; τdM - maximum dilation position, sec; τdr – time of dilation recalescence (contraction curve), sec; τer - time of eutectic recalescence (cooling curve), sec; τt – time between mould filling and the end of solidification, sec; (Δτ)ES - the disparity between the moments of the end of solidification indicated by first derivatives of cooling and contraction curves; FDES - minimum values of the first derivative of cooling curves at the end of eutectic solidification, °C/s; FDESC - minimum values of the first derivative of contraction curves at the end of eutectic solidification, %/s; (εd)i max - maximum initial expansion value, %; (εd)i TEN - expansion at the initial start of eutectic freezing (nucleation), %; (εd)i TES - expansion in the final moment of eutectic freezing, %; (εd)i ES - expansion value at the end of eutectic solidification established by the first contraction curve derivative, %; εap - contraction prior to pearlite transformation, %; εdp – the pearlitic dilation, %; TEM(e) – maximum rate of eutectic dilation, %/s; MP - the main derivative peak position relative to TL (before TL, it is positive), sec; Ir(e) - first derivative integral of the contraction curve during eutectic dilation; It(s) – total integral of the first contraction curve derivative (prior to pearlitic contraction) concentrated shrinkage, as a volume.

**Figure 3.** Scheme of cooling / contraction curves of ductile iron and their first derivatives.

The volume of cast samples, with covered and uncovered open concentrated shrinkage was measured. The apparent density as a result of open concentrated shrinkage and total shrinkage was
calculated, after weighing the samples. (c) A sample weighing method in both air and water was used to evaluate the apparent density due to the influence by total shrinkage in the region where all shrinkage types are present (\(\rho_{1}\)); also the apparent density as a result of only micro-shrinkage effect (\(\rho_{2}\)) in the region where only micro-shrinkage could be present in apparently sound samples. Apparent density (\(\rho_{1}\)) was evaluated by weighing the section of CCCA bar where both concentrated and macro-dispersed shrinkage were identified by X-Ray examination (it was assumed that a sample would also contain micro-dispersed shrinkage in this region). Apparent density (\(\rho_{2}\)) was also determined by weighing the section of CCCA bar where no concentrated or macro-dispersed shrinkage were found by X-Ray examination.

3. Results and comments

The final chemical composition of all inoculated ductile irons was within a very narrow range (wt.%): 3.71-3.76 C, 2.57-2.63 Si, 0.08-0.11 Mn, 0.022-0.023 P, 0.010-0.012 S, < 0.005 Ce, CE= 4.52-4.57%. All cast irons had relatively high final magnesium levels (Mg_{es}=0.065-0.075 wt.%) in order to emphasize the shrinkage sensitivity of the cast iron. A low content of other residual elements, typically (wt.%) 0.05 Cr, 0.03 Ni; 0.07 Cu; 0.067 Mo; 0.006 Ti; < 0.001 V; < 0.002 W; 0.003 Co; 0.010 Al; 0.007 As; 0.005 Sn; < 0.003 Sb; 0.0042 B; 0.0005 Bi; < 0.001 Nb; 0.001 Pb; Te < 0.002 excludes them as possible factors related to shrinkage.

Two major effects of minor elements were considered on the cast iron structure, mainly in ductile iron, in conjunction with base chemistry: pearlite promotion and anti-nodularizing effect. According to Thielman [15], pearlite promotion factor (\(P_{\pi}\)) and antinodularising factor (K) were calculated:

\[ K = 4.4 (\% Ti) + 2.0 (\% As) + 2.4 (\% Sn) + 5.0 (\% Sb) + 290 (\% Pb) + 370 (\% Bi) + 1.6 (\% Al) \]  (1)

\[ P_{\pi} = 3.0 (\% Mn) - 2.65 (\% Si - 2.0) + 7.75 (\% Cu) + 90 (\% Sn) + 357 (\% Pb) + 333(\% Bi) + 20.1 (\% As) + 9.60 (\% Cr) + 71.7 (\% Sb) \]  (2)

Typically, these irons have a low anti-nodularising influencing factor K=0.55 and a medium level of pearlite promoting factor \(P_{\pi}= 4.15\). It could be concluded that the content of anti-nodularising elements in both Mg-treated irons is low enough, so the role of rare earths to counteract these elements is limited. The pearlite factor \(P_{\pi}\) indicates a pearlite forming sensitiveness, for conventional solidification conditions. Structure characteristics are in accordance to the final chemical compositions of Mg-treated and inoculated ductile irons and the specific solidification conditions in the test bars of cooling/contraction curve analysis equipment: more than 80% graphite nodularity, 100 – 175 nodule count [1/mm²], 25 – 30% pearlite, 70 - 75% ferrite, no free carbides presence.

The thermal analysis evaluation (see figure 3) mainly considered some important temperatures on the cooling curves of cast irons, such as TGL - temperature of the liquidus (zero point on the first derivative), TSEF-temperature of the start of eutectic freezing (minimum negative on the first derivative at the beginning of solidification), TEU - the lowest eutectic temperature (zero point on the first derivative), TER - temperature of graphitic recalescence and TES - temperature of the end of solidification (minimum on the first derivative at the end of solidification). The level of these temperatures is usually compared to the equilibrium temperature, in stable / graphitic [Tst] and in metastable / carbide [Tmst] systems. There are many elements which individually have favourable or unfavourable influence on the equilibrium temperatures. Silicon appears to be the most important influencing element in un-alloyed irons especially at very low content of trace elements [Tst = 1153 + 6.7 (\%Si); Tmst = 1147 – 12 (%Si)] [16]. In the present program, \(\Delta T_s = Tst - Tmst = 54 – 56^\circ C\), according to high silicon content in final ductile irons.

Conventionally, undercooling is defined with reference to the graphitic equilibrium eutectic temperature (Tst), as \(\Delta T_m = Tst - TEU\). Free carbides occurrence is typically for \(\Delta T_m > \Delta T_s\) or TEU.
< Tmst condition, respectively. The importance of the position of the start of eutectic reaction (TEU) comparing to metastable (white) eutectic temperature (Tmst) is revealed by $\Delta T_1 = \text{TEU} - \text{Tmst}$. For the end of eutectic reaction temperature, $\Delta T_2 = \text{TER} - \text{Tmst}$ parameter was introduced. Free carbides formation is initiated by $\Delta T_1 < 0$, while graphite presence by $\Delta T_2 > 0$. Carbide formation structure is characterized by $\Delta T_1 < 0$ and $\Delta T_2 < 0$, mottled [graphite + carbide] structure is formed for $\Delta T_1 < 0$ and $\Delta T_2 > 0$ conditions, while a graphitic structure [without free carbides] could be formed only for $\Delta T_1 > 0$ and $\Delta T_2 > 0$ conditions.

Thermal analysis results confirm the real obtained structural parameters. $\Delta Tm = 15 – 19{\degree}C < \Delta Ts$, $\Delta T_1 = 35.8 – 40.1{\degree}C > 0$ and $\Delta T_2 = 37 – 42{\degree}C > 0$ illustrate a structure without free carbides content and a graphitic structure, respectively.

Intercellular carbides or/and inverse chill formation is dependent on the position of the temperature of the end of solidification (TES), compared to the metastable (white) eutectic temperature (Tmst), expressed by $\Delta T_3 = \text{TES} - \text{Tmst}$ parameter. Beneficial end of solidification means high solidus temperature and low level of the $\Delta T_3$ parameter (usually at low negative value, as TES < Tmst in the most of cases). In actual experiments $\Delta T_3 = -2…-15{\degree}C$ was obtained.

As cooling curve representative parameters, undercooling at the end of solidification [$\Delta T_3$] appears to have a visible influence on the contraction defects of ductile iron castings, especially as shrinkage formation and affected apparent density of castings (figure 4).

More negative $\Delta T_3$, higher shrinkage sensitiveness and lower casting density, respectively, for both tested mould media [soft green sand mould and rigid resin sand mould]. The relationship between the concentrated shrinkage volume level and undercooling at the end of solidification is strong [$R^2 > 0.97$], in both cases.

For the same undercooling at the end of solidification, shrinkage formation sensitiveness is visible influenced by the rigidity of the mould [higher for soft green sand mould]. The apparent density of ductile iron castings is more depending on the rigidity on the mould, comparing to the undercooling of the end of solidification [$R^2 = 0.34 – 0.49$].

As normally, apparent density in the casting regions where all of shrinkage types were present is lower than for only micro-shrinkage presence, but at higher dependence on undercooling at the end of solidification.

![Graph showing the relationship between undercooling and shrinkage volume and density](image)

**Figure 4.** Influence of the undercooling of the end of solidification [$\Delta T_3$, $^\circ$C] on concentrated shrinkage volume $C_{shv}$ (a) and apparent density $\rho$ (b) of inoculated ductile iron [GSM–green sand mould; RSM – resin sand mould; $\rho_1$ - all shrinkage type; $\rho_2$ – only micro-shrinkage presence].
Figure 5. Influence of mould hardness [rigidity] on the $\varepsilon_{\text{di, max}}$ [a], Ir(e) [b] and It(s) [c] contraction curves parameters of inoculated irons [GSM – green sand mould; RSM – resin sand mould].
Figure 6. Influence of the maximum initial expansion (a, b), the first derivative integral of the Contraction curve during eutectic dilation (c, d) and the total integral of the first contraction curve derivative, prior to pearlitic contraction (e, f) on concentrated shrinkage volume Cshv (a, c, d) and apparent density $\rho$ (b, d, f) of inoculated ductile iron [GSM – green sand mould; RSM – resin sand mould; $\rho_1$ – all shrinkage type; $\rho_1$ – only micro-shrinkage presence].
Three parameters on the contraction / expansion curves appear to be influenced by mould media rigidity (figure 5), with visible effects on the contraction defects formation (figure 6) in ductile iron castings, such as maximum initial expansion \( [(\varepsilon_{d}\text{max})] \), the first derivative integral of the contraction curve during eutectic dilution \( \text{Ir(e)} \) and the total integral of the first contraction curve derivative up to the end of contraction prior to the start of pearlite formation (eutectoid) \( \text{It(s)} \) as previous papers have pointed out [12–15].

Lower mould rigidity [Dietert hardness], higher maximum initial expansion level (a short time before the end of eutectic solidification), 0.5 – 0.8% for green sand mould [GSM] and 0.15 – 0.30% for resin sand mould [RSM], as figure 5a shows, for a high relationship rule \( [R^2 > 0.8] \). Similarly the first derivative integral of the contraction curve during eutectic dilution \( \text{Ir(e)} \) was influenced \( [R^2 > 0.85] \) (figure 5b). The total integral of the first contraction curve derivative (up to the end of antepearlitic contraction), \( \text{It(s)} \) is very strongly affected by mould type (figure 5c). This parameter has positive values on GSM and negative values on FRM pouring. So, by increasing of mould rigidity, \( \text{It(s)} \) sign is changed from positive to negative values. On a constant value of antepearlitic contraction \( \varepsilon_{d}\text{max} \), the \( \text{It(s)} \) value is in direct connection with \( \varepsilon_{d}\text{max} \), and by this way, a good correlation between \( \text{It(s)} \) and ductile iron shrinkage tendency could be found.

As a representative parameter, the maximum initial expansion \( [(\varepsilon_{d}\text{max})\%] \) was found to have a strong influence on shrinkage and micro-shrinkage formation in ductile iron castings, as Figures 6a and 6b show: higher \( \varepsilon_{d}\text{max} \), higher shrinkage sensitiveness and lower apparent density of the obtained ductile iron castings. Generally, the mould rigidity has an obvious effect on ductile iron shrinkage tendency. Both concentrated and total shrinkage were greatest in green sand mould (GSM) solidification, where there was much higher initial eutectic expansion \( \varepsilon_{d}\text{max} \) than in resin sand mould (RSM). Consequently, the apparent density of ductile iron samples was higher in RSM versus GSM. The GSM and RSM mould media are differentiated more by the contraction / expansion curve analysis results, such as the \( \varepsilon_{d}\text{max} \) parameter, in contrast to cooling curve parameters.

As also the first derivative integral of the contraction curve during eutectic dilution \( \text{Ir(e)} \) and the total integral of the first contraction curve derivative (up to the end of antepearlitic contraction), \( \text{It(s)} \) were influenced by mould rigidity, a good relationship between contraction defects sensitiveness and the level of these two important parameters on the contraction / expansion curves were observed (figures 6c,d and 6e, f). Higher \( \text{Ir(e)} \) and \( \text{It(s)} \) levels, typically for green sand mould, higher concentrated shrinkage volume \( \text{Cshv} \) \( [R^2 > 0.7] \) and lower apparent density of castings, for both evaluated situations: the lowest in the casting regions where all of shrinkage types were present \( [R^2 = 0.35 - 0.42] \) comparing to the regions were present than for only micro-shrinkage presence \( [R^2 > 0.7] \).

4. Conclusions

The obtained technique for simultaneous cooling / contraction / expansion analysis is useful to evaluate the sensitiveness of iron castings to form contraction defects, such as macro-shrinkage and micro-shrinkage.

This technique, incorporating two moulds, was used to test different inoculants, different inoculant additions, different mould media, and different iron chemistries, in laboratory experiments.

The mould rigidity has an obvious effect on the ductile iron shrinkage tendency. The highest level of both concentrated and total shrinkage was recorded in green sand mould solidification where a much higher level of the initial eutectic expansion \( \varepsilon_{d}\text{max} \), as compared to furan resin mould was recorded.

With higher maximum initial expansion (shortly before the end of eutectic solidification) and / or greater undercooling (more negative) at the end of solidification, there is an increase in concentrated and dispersed shrinkage volumes, which lowers the apparent density of ductile iron castings.

The dual purpose technique is easy to apply in the melt shop, similar to current thermal analysis systems. Using specialized software, both cooling and contraction / expansion curves and their pertinent readings are able to be displayed simultaneously.
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