Control of Solidification Pattern of Cast Irons by Simultaneous Thermal and Contraction / Expansion Analysis

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Abstract. An experimental device conducts thermal analysis and volume change measurements in a single ceramic cup with cast iron quality as the variable. The recorded data are processed using specialized software. Experiments compare solidification patterns for white [WI], grey [GI] and ductile [DI] irons, to correlate the most important events between the cooling curves and contraction curves, to evaluate the sensitivity to shrinkage formation. All of the irons have similar values for initial expansion up to the start of eutectic freezing [0.437 – 0.443%]. Graphite formation promotes expansion [WI - 0.002%, GI - 0.109%, DI - 0.596%], resulting a difference in the reached maximum expansion [WI - 0.465%, GI - 0.552%, DI - 1.032%], placed between the end of eutectic recalescence and the end of solidification. Higher graphite expansion, greater the shrinkage sensitivity; open shrinkage increased while the density of a casting when considering total shrinkage and micro-shrinkage formation decreased. Prolonged graphitization at the beginning of eutectic reaction increased the expansion and, consequently, shrinkage sensitivity. More graphite formation at the end of this stage also increased expansion, but this phenomena contributed to reduce of shrinkage level, due to the better access of liquid iron to compensate contraction holes. Special metallurgical treatments can favour a strong graphitization process at the end of solidification, with beneficial effects on the castings soundness.

Keywords: white, grey and ductile cast irons; solidification; thermal analysis; cooling & contraction curves; graphite expansion; shrinkage

1. Introduction

Contraction defects, such as macro and micro-shrinkage usually characterize iron castings, depending on the solidification pattern, specifically for carbides or graphite precipitation during solidification and graphite morphology type, too. Micro-shrinkage formation in inter-eutectic cells region is also favoured by a strong segregation of carbides-promoting elements in these regions.

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 characteristics [morphology, count, size], carbides [amount and distribution] and eutectic cells [size, count, distribution] characteristics, pouring temperature, metallurgical treatments [spheroidising and inoculation] act as the most important factors influencing the contraction defects. [1-9]

Thermal analysis testing, involving the cooling curve itself, as well as its derivatives and related parameters becomes an indicator of cast iron quality. It is important to measure the energy signatures of different phases and structures in cast iron and interpret them into usable chemistry and microstructure readings. Solidification thermal [cooling curve] analysis by thermocouple positioned in the mould was combined with the measurement of linear displacement during solidification by different techniques to obtain more information on solidification pattern and iron castings.
characteristics. Using specialized software, both cooling and contraction / expansion curves and their pertinent readings are able to be displayed simultaneously. [9 - 20]

The main objective of the present paper is to summarize the performance of this equipment illustrated by representative shrinkage tendency results in ductile iron as affected by mould rigidity (green sand and furan resin sand moulds), and its adaption for commercial foundry use, by comparing the solidification patterns for white, grey and ductile cast irons, focusing on the early stages of solidification, previously published in part. New data added, to deeply correlate the most important events between the cooling and contraction curves, to evaluate the sensitivity to shrinkage formation.

2. Background
In previous laboratory experiments [9 – 12, 19], a technique incorporating two moulds was used to test different inoculants (FeSi-based alloys, including in different variants Ca, Ba, Zr, Al, Ce, S, O), different inoculant additions, different mould media (green sand and furan resin sand moulds), and different iron chemistries (hypo and hyper-eutectic compositions). The ductile iron shrinkage sensitivity is mainly depending on the mould rigidity. A much higher level of eutectic expansion \((e_{di})_{\text{max}}\) was obtained in green sand mould, as compared to furan resin mould, and consequently, the highest level of both concentrated and total shrinkage was recorded (Fig. 1). With higher maximum initial expansion (shortly before the end of solidification) and/or greater under-cooling (more negative) at the end of solidification, there is an increase in concentrated and dispersed shrinkage volumes, which lowers the apparent density especially of ductile iron castings. [19]

Fig. 1. Arrangement of twin mould cooling and contraction / expansion curves analyser (CCCA) (a) and maximum initial expansion \([e_{di}]_{\text{max}} \times 10, \%\), concentrated shrinkage volume \([\text{Cshv}, \text{vol.} \%\]), concentrated \([\text{Cshs}, \text{cm}^2\]) and total \([\text{Tshs}, \text{cm}^2\]) shrinkage surface and apparent density \([\rho_1, \text{g/cm}^3\]) of inoculated ductile irons solidified in green sand moulds (GSM) and resin sand moulds (RSM) (b). [11]

3. Experimental procedure
The dual purpose technique was adapted to apply in the melt shop, similar to current thermal analysis systems (Fig. 2a). [11] The intent was to provide a simple-to-use system for comprehensive evaluation of treated iron quality, as the variable, under the same mould media solidification conditions. A special ceramic cup was designed, to include a thermocouple (for cooling curve analysis) and a device for contraction and expansion curve analysis. A shell mould was formed using phenol-formaldehyde resin (Novolak) coated sand (Croning process), with a high rigidity (cca. 95 Dieter Hardness number). This sample (750g) is characterized by a cooling modulus (CM) of 0.70cm, close to the standard ceramic cup – Quik-cup™ (0.75cm). This equipment was upgraded for more accuracy data registration, including a high speed type PCI-6284 interface to record simultaneous temperature and linear displacement data. [13] Recently [13, 20] this equipment was used to compare solidification pattern of hypo-eutectic grey [GI] and ductile [DI] irons with white [WI] iron as reference.
Fig. 2 Cooling and contraction / expansion curve analyser (a) and typical Cooling Curve \[ T = f(t) \] and its first derivative \[ \frac{dT}{dt} = f(t) \] and contraction curve \[ \varepsilon = f(t) \] and its first derivative \[ \frac{d\varepsilon}{dt} = f(t) \] for ductile cast iron solidification. [TAL-temperature of austenitic liquidus, 0°C; TSEF-temperature of the start of eutectic freezing (nucleation), 0°C; TEU-temperature of the maximum eutectic undercooling, 0°C; TER-temperature of eutectic recalescence, 0°C; TES temperature of the end of solidification, 0°C; A-position on the contraction curve corresponding to TSEF moment (the beginning of the intensive eutectic graphitization); \( \varepsilon_{di}(TSEF) \)–expansion before the start of eutectic freezing, %; \( \varepsilon_{di}(max) \)–maximum expansion, %; \( \varepsilon_{di}(TES) \)–expansion at the end of solidification, %; \( \varepsilon_{di}(gr) = \varepsilon_{di}(max) - \varepsilon_{di}(TSEF) \), graphitic expansion, %; B-maximum value of the graphitic expansion acceleration].

Experimental grey and ductile cast irons were obtained by standard procedures, including inoculation for grey irons (0.15wt.% Sr-FeSi alloy, ladle treatment) and double treatment for ductile irons (a tundish cover nodularization technique, 2.0wt.% FeSiCaMgRE alloy followed by 0.5wt.% Ca, Ce, S, O-FeSi alloy, ladle inoculation). By Te-addition to the grey iron melt into the ceramic cup of cooling-contraction analysis equipment, before solidification, a non-graphitic (carbidic) structure resulted, or white (WI) cast iron, respectively. Hypo-eutectic cast irons were considered for these experiments, according to obtained carbon equivalent (CE) level: CE = 3.56 – 3.77% for grey cast irons, CE = 3.98 – 4.11% for ductile cast irons and CE = 3.62 - 3.64% for white cast irons.

The experiments were repeated, [2 samples for each heat] with 8 heats tested for grey irons, 5 heats for ductile irons and 2 heats for white irons. Each heat was controlled to ensure similar thermal and chemistry histories. The cast iron chemistries for the base chemical composition and level of minor elements were evaluated in the base irons and treated irons by the use of a performance spectrometer (SPECTROLAB M 10, Hybrid Optic) capable of determining very low levels of minor elements.

4. Results and Discussion
Figure 2b shows a typical assembly of simultaneous recorded solidification cooling and contraction curves, including their first derivatives. Previous preliminary reported results (Fig. 3) [13, 20] illustrate specific behaviour of the tested cast irons, as cooling and contraction / expansion parameters.
Grey cast iron castings [GI] are characterized by greater undercooling during the eutectic reaction referring to the metastable (Tmst) equilibrium eutectic temperature, in iron-carbide system diagram [lower $\Delta T_1 = \text{TEU} - \text{Tmst}$ and $\Delta T_2 = \text{TER} - \text{Tmst}$], while ductile iron castings [DI] shown a greater (more negative) undercooling at the end of solidification [$\Delta T_3 = \text{TES} - \text{Tmst}$] (Fig. 3a).

All of the tested cast irons have similar values for initial expansion up to the start of eutectic freezing [$\varepsilon_{\text{di (TSEF)}} = 0.44\%$] due to the ferro-static pressure, silica sand mould expansion, mould movement etc. A-point (Fig. 2b) illustrates the separation between the mould expansion and graphitic expansion. The maximum expansion [$\varepsilon_{\text{di (max)}}$], reached between the end of the eutectic recalescence and the end of solidification, depends on the carbides / graphite ratio and graphite morphology: WI-0.465%, GI-0.552%, DI-1.032%, as averages. Graphitic expansion [$\varepsilon_{\text{di (gr)}}$] absent for WI, increased to 0.109% [GI] and up to 0.596% [DI]. For both GI and DI the expansion at the end of solidification [$\varepsilon_{\text{di (TES)}}$] is only 6% lower compared to the maximum level, while for WI it decreased more than 50% because of matrix contraction (Fig. 3b).

Specifically the acceleration rate of the graphite expansion up to the maximum level [$K_{gr1}$] is different compared to its deceleration to the end of solidification [$K_{gr2}$], and also are different for irons being tested, GI versus DI. These parameters were defined in a previous paper [13] by the difference in expansion [$\varepsilon_{\text{di}}$], in decreasing temperature [$\Delta T$] and increasing time [\$\Delta t\$] values in these two sections [$K_{gr} = \Delta \varepsilon_{\text{di}} / (\Delta T \times \Delta t), \mu \text{m/s.}^\circ\text{C}$]. Nodular graphite led to the [$K_{gr1}$] being 2.5 times higher, compared to GI, whereas only a slight difference was observed between GI and DI for the $K_{gr2}$ (Fig. 3c,d).

There were found good relationships between graphite expansion [$\varepsilon_{\text{di (gr)}}$] and both specific factors $K_{gr1}$ and $K_{gr2}$ for grey cast irons: higher $\varepsilon_{\text{di (gr)}}$, higher $K_{gr1}$, but lower $K_{gr2}$. For ductile irons, the same relationships present some irregularities: higher expansions, higher $K_{gr1}$ factor, or the acceleration of expansion up to the maximum values, in the same way as in grey iron, but with less dependency. The $K_{gr2}$ factor does not appear to be in a clear relationship with both $\varepsilon_{\text{di (gr)}}$ and $\varepsilon_{\text{di (max)}}$ expansions.

Higher graphite expansion in DI led to higher shrinkage sensitiveness than in GI, as measured in
furan resin mould test castings: open shrinkage increased \([\text{Sh} = 1.99 \, \text{cm}^3/\text{kg} \, (\text{GI}) \, \text{versus} \, 4.33 \, \text{cm}^3/\text{kg} \, (\text{DI})]\) while the real density of a casting when considering total shrinkage and micro-shrinkage formation decreased \([\rho = 7.18 \, \text{kg/cm}^3 \, (\text{GI}) \, \text{versus} \, 6.73 \, \text{kg/cm}^3 \, (\text{DI})]\) (Fig. 4a). More analysis on the obtained results led to the summarized data in Figures 4b,c,d. Increasing of the acceleration rate of the graphitic expansion up to the maximum level \([K_{gr1}]\) promoted an increasing of the shrinkage sensitiveness, expressed by decreased real density due to the presence of contraction defects. Contrary, higher deceleration to the end of solidification \([K_{gr2}]\), lower shrinkage sensitiveness for both irons.

Not only the graphite expansion \(\varepsilon_{di(\text{gr})}\) and resulted maximum expansion level \(\varepsilon_{di(\text{max})}\) are important to determine the level of shrinkage and micro-shrinkage, but also the solidification characteristics during the maximum expansion landing process. Increasing the length (time) of the expansion at the maximum level \(\Delta t[\varepsilon_{di(\text{max})}]\) favours the shrinkage formation, as the result of the increasing of the graphitic force on the mould walls (Fig. 4c). The same effect was registered as the effect of the specific temperature drop during the maximum expansion landing time \(K[\varepsilon_{di(\text{max})}]\) (Fig. 4d). Experiments pointed out that the graphite expansion has two contrary effects during graphite formation process. Increased graphite expansion (force) led to higher shrinkage sensitiveness at the first part of eutectic reaction (Fig. 4a), but to the decreasing of shrinkage at the end of solidification, due to the forcing of the last liquid iron to occupy the previous formed cavities.

From the practical point of view, it is important to apply special metallurgical treatments to favour a strong graphitization process at the end of solidification. The test data acquired offer a possible explanation of other reported results [2, 3, 9-11] on reduced shrinkage tendency in ductile iron castings when using Ce,Ca,S,O-FeSi inoculation or La-MgFeSi nodularisation treatment. This is attributed to a bimodal or skewed nodule size distribution (fewer large nodules formed at the start of solidification and a high number of much smaller nodules formed later, towards the end of solidification).

![Graph showing the influence of graphite expansion value](image1)

![Graph showing the influence of specific factors](image2)

![Graph showing the influence of maximum expansion landing time](image3)

![Graph showing the influence of temperature drop during expansion landing time](image4)

**Fig. 4** Influence of graphite expansion value (a), specific factors \(K_{gr1}\) and \(K_{gr2}\) (b), maximum expansion landing time \(\Delta t[\varepsilon_{di(\text{max})}]\) (c) and the temperature drop during the expansion landing time \(K[\varepsilon_{di(\text{max})}]\) (d) on the shrinkage sensitiveness expressed by open shrinkage (Sh) and real density (\(\rho\)).
5. Conclusions
*A ceramic cup variant of the dual technique [simultaneous cooling / contraction analysis], with constant mould media and with recorded data processed using specialized software was obtained to apply in the melt shop similar to current thermal analysis systems;
All of the irons have similar values for initial expansion up to the start of eutectic freezing [cca 0.44%]; graphite formation promoted expansion [WI-0.002%, GI-0.109%, DI-0.596%], and, consequently, different maximum expansion [WI-0.465%, GI-0.552%, DI-1.032%], and higher shrinkage sensitivity for ductile irons, respectively;
Increasing of the acceleration rate of the graphitic expansion up to the maximum level [K_{gr1}] promoted an increasing of the shrinkage sensitiveness (decreased real density). Contrary, higher deceleration to the end of solidification [K_{gr2}], lower shrinkage sensitiveness for both irons;
Increasing the length (time) of the expansion at the maximum level \Delta t_{[di(max)]} favours the shrinkage formation, as the result of the increasing of the graphitic force on the mould walls;
Experiments pointed out that the graphitic expansion has two contrary effects. Increased graphitic formation, as the result of the increasing of the graphitic force on the mould walls;
Increasing the length (time) of the expansion at the maximum level \Delta t_{[di(max)]} favours the shrinkage formation, as the result of the increasing of the graphitic force on the mould walls;
Increasing of the acceleration rate of the graphitic expansion up to the maximum level [K_{gr1}] promoted an increasing of the shrinkage sensitiveness (decreased real density). Contrary, higher deceleration to the end of solidification [K_{gr2}], lower shrinkage sensitiveness for both irons;
Strong graphitization process promotion at the end of solidification favours the castings soundness.

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