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Analysis of the thixoability of ASTM A536 ductile iron

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ABSTRACT

Purpose: Thixoability of the ASTM A536 nodular cast iron is analyzed, it meaning its ability to hold a thixotropic semi-solid state and to be formed as such. Thixoability can be characterized by the solidification range, fraction of primary phase and sensitiveness of liquid fraction with temperature (df_l/dT) within the solidification range. It is also investigated the effect of thixocasting in the microstructure of the considered alloy.

Design/methodology/approach: Differential thermal analysis, differential scanning calorimetry and thermodynamic calculation package THERMOCALC were used to predict transformations temperatures involving liquid formation and df_l/dT within the solidification range. Microstructures of thixotropic slurries produced by partial melting were observed.

Findings: Thixoforming of ASTM A536 nodular iron can be considered in a narrow window of about 28°C, were some dissolution of graphite nodules can still be afforded; this window meaning the range of temperatures of co-existence of austenite + graphite + liquid were the eutectic transformation is taking place. At higher temperatures the dissolution of graphite nodules in liquid can be significant.

Research limitations/implications: Thixoability prediction models rely on sensitive experiments as thermoanalysis, with results strongly dependent on experimental conditions; and on thermodynamic data, sometimes not available or reliable for a specific alloy composition.

Practical implications: The prediction of the thixoability of a certain alloy can make it more effective its thixoprocessing, allows better control of processing parameters and quality of final product; can also subsidize modifications in the alloy to make it more suitable to semi-solid processing.

Originality/value: The study of the thixoability of a nodular hypereutectic cast iron is an original subject, not available in the specialized literature, however absolutely necessary if thixoprocessing of this family of alloys is to be considered.

Keywords: Casting; Thixoability; Thixoforming; Semi-solid alloys

1. Introduction

With the progress of the semi-solid technology development along the years and the consequent familiarization with the control parameters of the thixotropic slurries fabrication and forming processes, researchers and costumers in the field have been finding consensus on some basic requirements for a specific alloy to be candidate to thixoforming processing. The potential ability of a certain alloy for thixoforming is characterized by its thixoability, which must gather some criteria such as the solidification range of the alloy, the liquid fraction at eutectic temperature, and the sensitivity of liquid fraction with temperature [1, 2]. The first criteria can be limited by the susceptibility of the alloy to hot cracking during cooling if the solidification range is too wide; concerning the second criteria, it has been observed that more controllable is the processing if eutectic reaction occurs at 30 to 50% liquid and third criteria states that df_l/dT can not be too abrupt, otherwise little changes in temperature lead to big variation in the liquid fraction and make it difficult to control the

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process. Results for Al-Si-Cu alloys [3, 4] indicate values of df_l/dT between 0.007 K^{-1} to 0.067 K^{-1} at f_l=0.4, depending on the Si-Cu content. It means that an increase of 1K in the alloy presenting 40% liquid implies in an addition of 0.7 and 6.7 in the fraction of liquid content (%) in the semi-solid; in the first case (only 0.7 increase in f_l/K) thixoability is higher, allowing easier manipulation of the alloy in the semi-solid state.

Given the more recent application of the semi-solid technology for ferrous alloys, when compared with the already commercial use of this technology for Al and Mg systems, a little has been done so far to establish the thixoability of such family of alloys. Some special classes of steels, such as stainless and tool series have been catching attention and some results can be available [5, 6]. However, as far as cast iron is concerned, very little information can be found in the specialized literature, in spite of the importance of such family of alloys and the potential advantages of using semi-solid technology. In one of the available technical papers [7] it is shown the possibility of producing thinner cast sections of gray iron, via thixocasting process.

This work investigates the thixoability of the nodular iron ASTM A536, which finds commercial application in the automotive industry as several cast components. The knowledge of the alloy thixoability can make more effective its thixoprocessing, allowing better control of processing parameters and quality of final product.

2. Experimental procedures

ASTM A536-60-40-18 (ISO 1693-400-15) nodular iron with chemical composition presented in Table 1 was used in this work. This alloy is a hypereutectic system, presenting at room temperature a cast structure containing ferrite and nodular graphite.

The experiments were divided in two series: study of the thixoability of the considered alloy and effective production of samples of thixotropic semi-solid for observations of microstructure in the thixocast condition.

For thixoability studies, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) tests were performed. Curves energy x temperature were taken during heating and cooling at two different rates: 5 and 10°C/min. From these curves, temperatures of phase transformations, mainly those involving liquid formation, and df_l/dT were obtained. To complement thixoability analysis, it was utilized the software THERMOCALC to generate the probable phase diagram for the specific composition used. Informations from the diagram were taken together with thermal analysis results to discuss the thixoability of the considered alloy. For THERMOCALC calculations it was assumed a heating rate of 1°C/min.

Samples of thixotropic semi-solid were produced by partial melting at different temperatures (from 1140 to 1161°C) and holding at a constant pre-defined temperature for 30 min followed by rapid cooling in water. Conventional metallography technique was used to prepare cross sections for microstructure observations; Nital 3% was the etching employed.

3. Results and discussions

3.1. Thermal analysis

During solidification of a hypereutectic Fe-C system, if Si content is high, the stable phase graphite is formed as primary phase in the liquid in the solidification range.

An important characteristic of Fe-C-Si systems is that eutectic transformation is not isothermal but takes place within a narrow range of temperatures, where austenite, graphite and liquid coexist, as shown in the general diagram from literature presented in Figure 1.

In the eutectic transformation austenite is formed in the carbon-depleted melt around graphite nodules, encapsulating the primary phase. As transformation proceeds, both graphite nodules and the newly formed austenite grow, maintaining the eutectic transformation $L \rightarrow \gamma + G$, not in a typical cooperative nucleation-growth, as no new graphite nodules are formed. In this particular case, the transformation is not isothermal but occurs in a narrow temperature interval. At lower temperatures, eutectoid transformation leads to the final structure of the alloy, presenting ferrite and graphite.

Thermal analysis shall help to identify solidification range of the analyzed alloy, it meaning two distinct regions: one where liquid and graphite phases are present, limited by T-liquidus and the temperature at which eutectic transformation initiates (T_5 to T_4 in Figure 1); and the eutectic region, where liquid + graphite + austenite are present, going from T_4 to T_3, when the eutectic transformation finishes.

Taking the cooling curve from liquid, for example, it should show the temperature at which primary solid (graphite) is nucleated, it meaning T-liquidus, the temperatures of eutectic reaction initiation, with the formation of austenite, and the finishing of

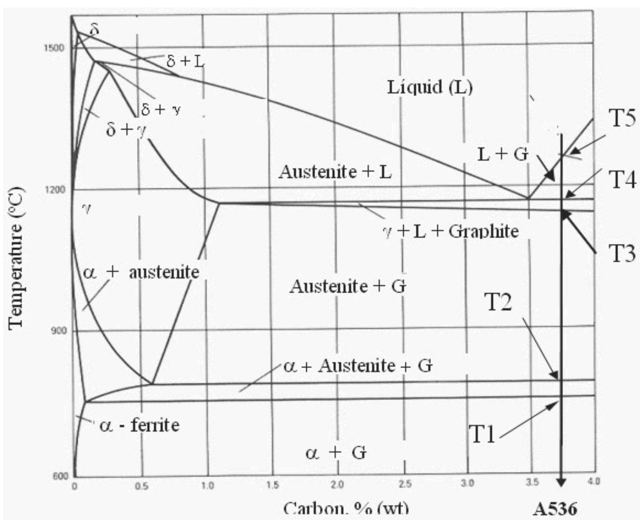


Fig. 1. General Fe-C-Si diagram (stable) for 2.5wt%Si from literature [8]

Table 1.
Chemical composition (wt%) of the ASTM536 cast iron used in the experiments

C	Si	Mg	Mn	P	S	Fe
3.74	2.98	0.05	0.19	0.006	0.01	balance

eutectic reaction or temperature at which no liquid remains, it meaning T-solidus. The total solidification range must be considered, therefore, the whole interval from f_{liq} = 100% to f_{liq} = 0% or from T_5 to T_3.

A typical result of thermal analysis of the ASTM A536 nodular iron studied is presented in Figure 2.

At low temperatures, it can be observed an inflexion at around 450°C (indicated as A), probably due to stress relief during heating. A more defined peak (B) can be observed around 820°C, which can be related to eutectoid transformation (austenite → ferrite + graphite). At higher temperatures, a transformation with significant variation of energy initiates at 1157°C (peak C), followed by small successive peaks until ~1358°C. Repeated tests show similar behavior: a well defined peak starting around 1145-1155°C followed by one or two not clearly defined and comparatively lower energy peaks at higher temperatures.

Data from literature [9] for Fe-C-Si systems indicates T-liquidus higher than 1300°C for alloys with C and Si contents as the ASTM 536.

Therefore, it can be supposed that the initial, high energy inflexion is associated to the eutectic transformation and the following small peaks to dissolution of graphite globules and eventual intermetallic phases in the liquid (regardless of their improbable presence for the considered composition).

As the composition of the considered iron is close to eutectic, during heating most of the liquid is formed in the eutectic

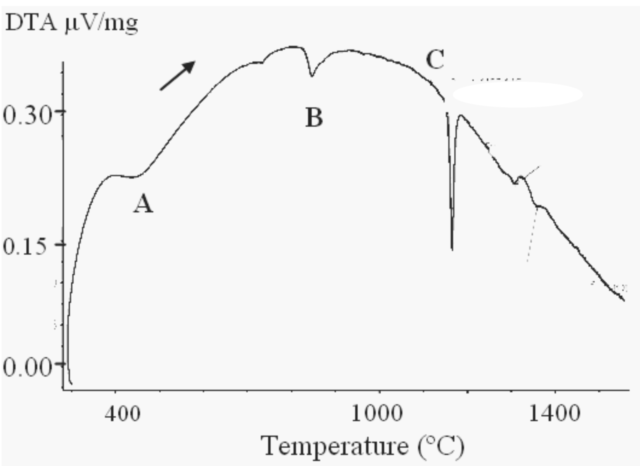


Fig. 2. DTA signal x T for ASTM A536 nodular iron. Heating rate: 10°C/min

transformation, or within the T_3-T_4 interval. In equilibrium conditions it means that 99.7% of liquid is formed by melting of the eutectic phase. Therefore, as far as thixoforming is concerned, the thixoability of the alloy is mostly defined by the sensitiveness of liquid fraction with temperature within this specific range (T_3 to T_4 indicated in the general diagram of Figure 1). At temperatures higher than T_4, solid fraction is small (light weight graphite nodules in dissolution) and it would be difficult to control the thixoforming processes. Furthermore, at those high temperatures the dissolution of graphite can be quick, what must be minimized to avoid deterioration of the characteristics of the nodular iron considered.

Therefore, the determination of the eutectic transformation range is fundamental to analyze the thixoability of the considered cast iron. DSC experiments were performed to pursuit this objective, as this sort of thermal analysis can be more sensitive to energy variations than ATD. Tests were carried out in different conditions of heating and cooling; several experiments were performed in the same test conditions to make the results more reliable, as DSC is very sensitive to experimental conditions such as sample mass, heating/cooling rate, oxidization of the sample, contact of the material with crucible and so on.

Typical DSC results are shown in Figure 3, for tests at two different heating conditions.

Fist of all, it can be observed the coincidence of the obtained curves, assuring the results reliability. It can be observed the two main inflexions related to eutectoid (peak B) and eutectic (peak C) transformations. Table 2 shows transformations temperatures given by the tangent method applied to the inflexion attributed to eutectic transformation detected in all curves produced – values presented correspond to the average for 2 distinct tests in the same condition.

Results obtained in different conditions are quite similar apart of the influence of cycle type: significant differences were observed between cooling and heating cycles; this is usually attributed to different conditions of contact between sample and crucible walls, either the sample is in solid or liquid state. The influence of heat transfer on transformations temperatures is less significant; however the intensity of energy variation in a specific transformation is higher in tests at the higher rate employed, due to more difficulty on heat transfer in this condition.

As thixoforming implies in heating of the material from solid to semi-solid state, it is reasonable to consider results obtained from heating experiments performed at 10°C/min, a condition less far from practical. Therefore, eutectic transformation can be assumed as taking place between 1140 and 1168°C, it meaning a narrow window of about maximum 28 degrees for semi-solid processing, what can make difficult the process control.

Table 2.
Transformations temperatures of ASTM A536 nodular iron, according to DSC analysis, for eutectic range

	Cycle type			
Temperature	Heating		Cooling	
	5°C/min	10°C/min	5°C/min	10°C/min
T_i (ºC)	1140	1140	1141	1140
T_f (ºC)	1161	1168	1122	1116

T_i – temperature where transformation initiates; T_f – temperature where transformation finishes

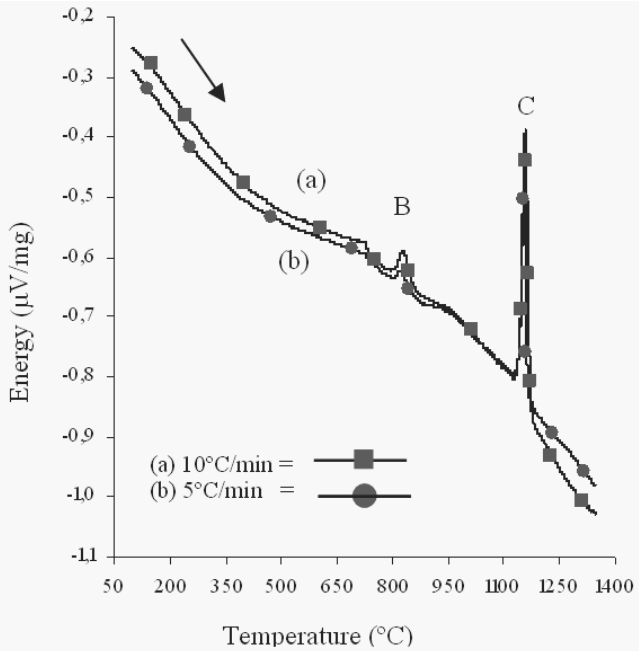


Fig. 3. DSC signal x T for ASTM A536 nodular iron; different heating rates: 10°C/min and 5ºC/min

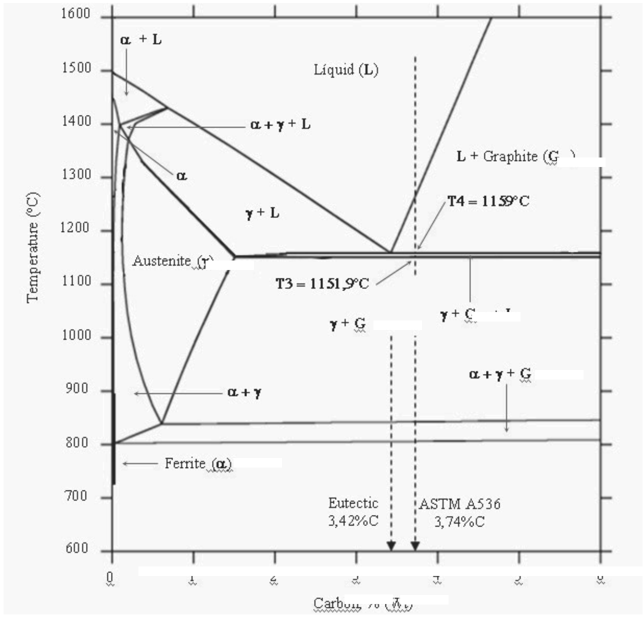
3.2. Phase diagram simulated by thermodynamic calculations

THERMOCALC commercial software was used to generate the phase diagram for the specific composition of the cast iron considered in the work; resulting general diagram and a magnified detail of the eutectic transformation are shown in Figure 4.

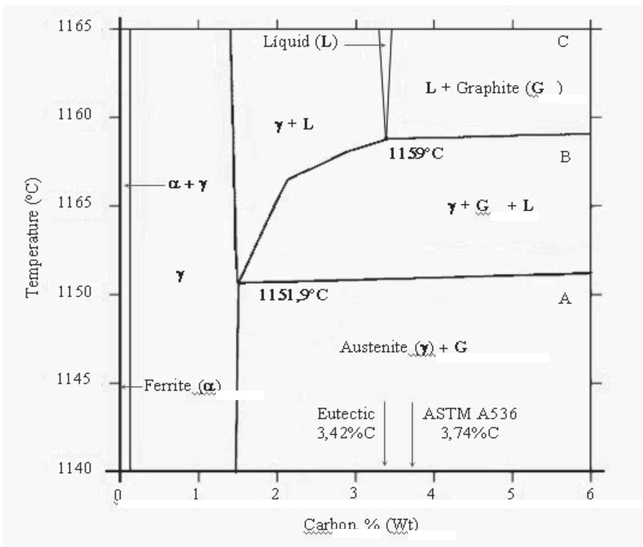
It can be observed that eutectic composition is 3.42wt%C; the two major phase transformations, eutectoid and eutectic, occur within a range of temperatures and involve three phases: during eutectoid transformation austenite + ferrite + graphite co-exist (therefore a ternary system) and, during eutectic transformation austenite, graphite and liquid are the phases present in the system.

Detail of eutectic range presented in Figure 4 (b) shows temperatures of 1152 and 1159°C as beginning and finishing of melting of eutectic phase in a heating procedure. This range is narrower than the eutectic transformation range detected in thermal analysis tests. Moreover, according to the generated phase diagram, T-liquidus of the considered cast iron is 1260°C; thermal analysis results did not indicate any transformation at this temperature. Therefore, values of transformations temperatures predict by thermodynamic calculation are lower than results obtained by thermal analysis; this discrepancy can be attributed to the low heat transfer rate considered in the thermodynamic calculations, closer to equilibrium conditions (1°C/min).

From obtained data, it was also determined the variation of liquid fraction with temperature, which is shown in Figure 5. As mentioned previously, as the composition of the studied alloy is close to eutectic, the liquid content in the system does not change significantly with temperatures from T_4 to T_5. It means that on heating, most of the liquid is formed by eutectic phase melting within the range of temperatures where eutectic transformation takes place (T_3 to T_4).



(a)



(b)

Fig. 4. Fe-C phase diagram generated by thermodynamic calculations for the composition analysed in this work (ASTM A536 nodular iron). (a) general; (b) detail of eutectic transformation. Heat transfer rate considered: (1°C/min)

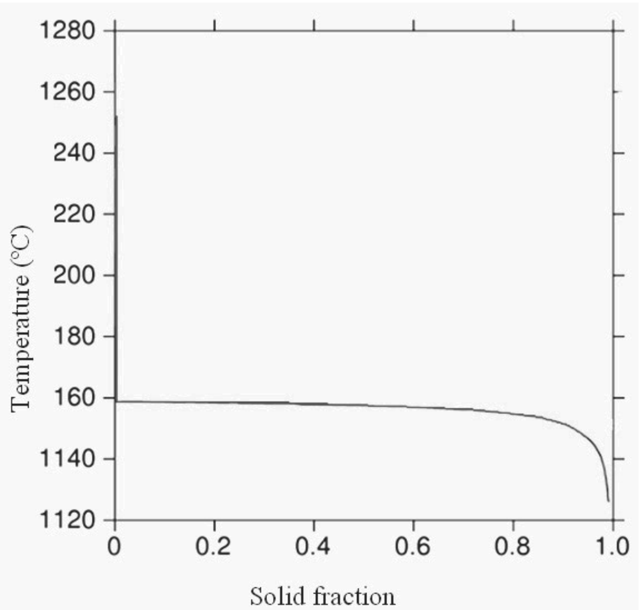


Fig. 5. Variation of solid fraction x T for ASTM A536 nodular iron, generated by THERMOCALC

Figure 5 shows clearly the massive formation of liquid at eutectic transformation range (region indicated by the green line), from the final of eutectic transformation the liquid fraction variation with temperature increase is negligible (region indicated by the red line; solid region is indicated by blue line).

3.3. Thixoability of ASTM 536

Taking in account that on heating ASTM A536 cast iron, most of the liquid is formed within the eutectic transformation interval, it was determined the variation of liquid fraction x T of the alloy by calculating the relative areas under the transformation peaks related to the eutectic transformation obtained in the DSC experiments. Therefore, it is assumed that the error induced by considering $f_l = 1$ at the end of the eutectic transformation (at T_4), and not at the actual T-liquidus (T_5 as indicated in Fig. 1), is negligible.

For each specific temperature within the beginning and the finishing of the transformation, it was calculated the relative area given by:

$$f_l\,(n) = \frac{\text{Partial area } A_n\,(T_n - T_i)}{\text{Total area } A_t\,(T_f - T_i)} \qquad (1)$$

where f_l (n) = liquid fraction at a generically T_n, is the relation between the area under the DSC curve limited by T_n and the temperature where liquid fraction is 0, or the temperature where transformation initiates (T_i); and the total area under the peak , or from temperature where transformation initiates and finishes (T_f).

Results are shown in Figure 6. Acceptable processing windows for thixocasting and thixoforming are suggested in the Figure. Processing window is the range between maximum and minimum liquid fraction where semi-solid can be reliably processed. In casting operations liquid fractions around 0.6 can be quite feasible, while for mechanical forming operations sometimes liquid fractions as low as 0.05 can be the limit, as for instance in drawing of Al alloys sheets in semi-solid state [10].

The variation of liquid fraction with temperature is not linear: is lower at the beginning and finishing of the transformation; the slope of the curve is higher exactly within the processing windows. So, thixoability material depends on the sensitity of df_l/dT at processing temperatures: liquid fraction shall not change drastically with temperatures, otherwise process control can become critical and even impossible.

Figure 7 presents calculated values df_l/dT for the A536 cast iron analyzed.

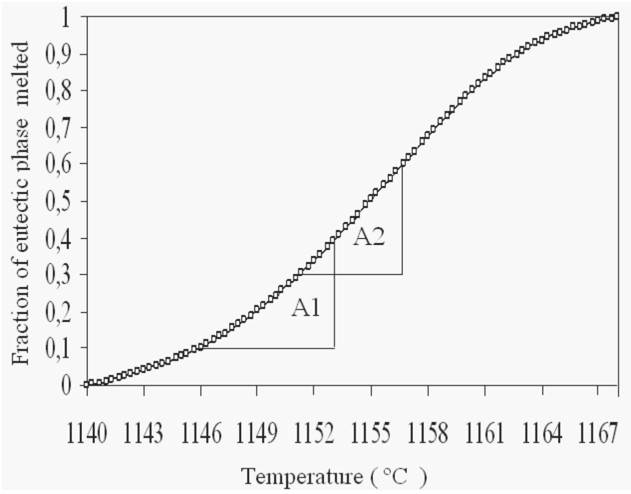


Fig. 6. Fraction of eutectic phase transformed in liquid x T on heating of ASTM A536 nodular iron. Suggested thixoforming windows (A2 for thixocasting; A1 for thixoforging)

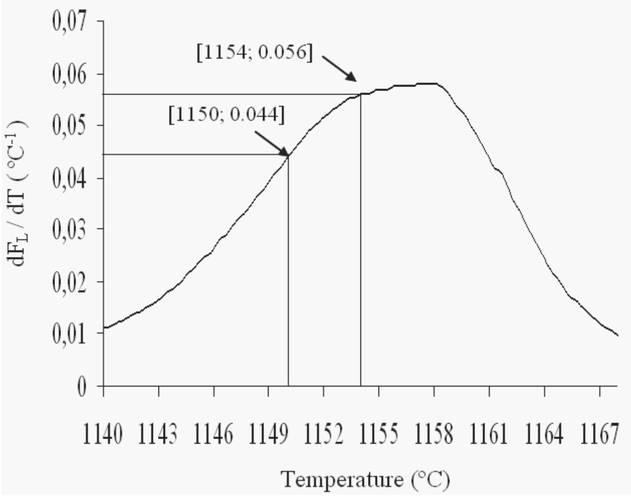


Fig. 7. Sensitivity of liquid fraction x temperature [df_l / dT] for ASTM A536 nodular iron. Points A and B: values for thixoforming at f_l = 0.25 [1150ºC] and f_l= 0.45 [1154ºC], respectively

It can be observed that df_l/dT is not linear, being higher at intermediate temperatures between beginning and finishing of the transformation. General results in the presented curve show that in the whole spectrum of values of temperatures or liquid fractions, df_l/dT varies from around 0.01 to $0.057C^{-1}$. In the specific range suggested for thixoforming two points where picked to exemplify the sensitivity of liquid fraction with temperature: points A and B in the curve indicate the values for typical thixoforming temperatures: $df_l / dT = 0.044C^{-1}$ and $0.056C^{-1}$ for $f_l = 0.25$ (at 1150ºC) and $f_l = 0.45$ (at 1154ºC), respectively. These values indicate the need of a close control of thixoforming temperature to insure the viability of the process.

Studies on Al-Si, Al-Zn-Mg-Cu alloys, considered as presenting good thixoformability, df_l/dT ranges from as low as $0.007C^{-1}$ [3, 11] as mentioned previously. As far as ferrous alloys are concerned, some literature information reveals values from 0.0097 to 0.02 for Cr-Mn alloy steels [12].

Therefore, thixoforming of ASTM A536 must be looked with care; however, taking in account the tight control of temperature on re-heating of billets for thixoforming already achievable using commercial softwares for induction heating, processing the studied cast iron in the semi-solid state, although requiring attention, can be considered.

3.4. Thixocast microstructures produced by partial melting

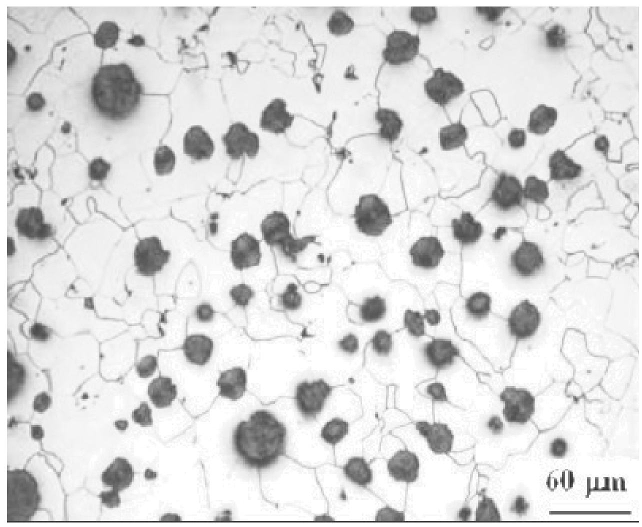
Semi-solid samples of the studied alloy were produced by partial melting at temperatures within the pre-determined eutectic range. Typical resulting microstructure is shown in Figure 8 (b); while (a) shows the original as-cast condition. Thixocast material presents globular phase, in this case coarse grains of lamellar martensite, interglobular fine martensite and remaining graphite spheroids. Globular grains of martensite indicates globular austenite phase in the semi-solid state, transformed to martensite by the rapid cooling imposed to the thixotropic slurry.

It can also be observed significant increase in the size of austenite grains caused by re-heating and holding at high temperatures. To obtain a semi-solid with thixotropic characteristics, a proper spheroidization of a solid phase in liquid environment at thixocast temperatures is required; this phenomena involves diffusion and, therefore, is time dependent. On the other hand, diffusion can also promote undesirable growth of solid phases by coarsening, coalescence, ripening etc., as observed here and described elsewhere [13]. This effect must be prevented to avoid excessive growth with consequent deterioration of rheological properties of the semi-solid. As austenitic grains are already nearly globular, in this case faster heating rate and shorter holding times must be preferentially used.

Concerning the graphite phase, it is observed the reduction in number and dimensions of the globules in the thixocast material, compared to the as-cast condition, due to their dissolution in the liquid at the thixocast temperature.

Quantitative analysis of the graphite phase present in ASTM A536 iron thixocast at different temperatures was performed to evaluate the extent of graphite dissolution. Results are shown in Figure 9 and 10: a reduction of the globules number as well as their dimension, as thixocast temperature increases. Maximum reductions around 20% and 40% in number and dimension of globules, respectively, are observed when heating at the maximum thixocast temperature.

Taking in account the large holding time of the experiments (30 min), the dissolution of the graphite, although an effect to be carefully monitored during thixocasting of nodular iron, shall not constitute a limitation for semi-solid processing of such alloys. Faster heating and shorter holding time at high temperatures can avoid excessive graphite dissolution with consequent de-characterization of the material properties.



(a)

(b)

Fig. 8. Microstructures of ASTM A536 nodular iron; (a) as–cast; (b) thixocast by re-heating and holding at 1157°C/30 min

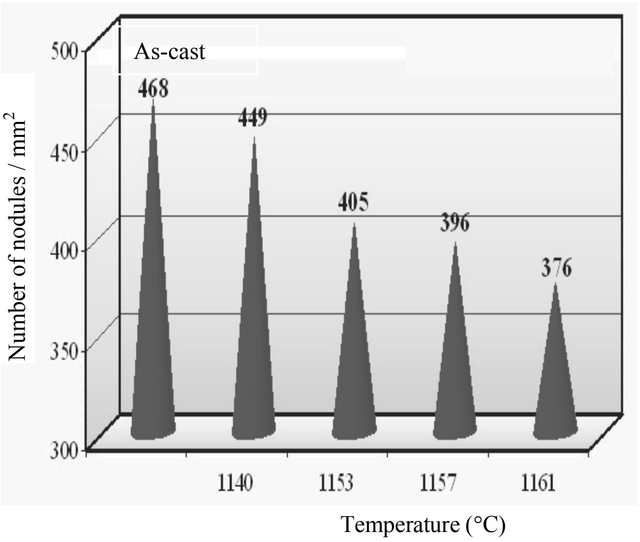


Fig. 9. Variation of number of graphite nodules x thixocast temperature, for ASTM 536 nodular iron. (Holding time at the specific temperature: 30 min)

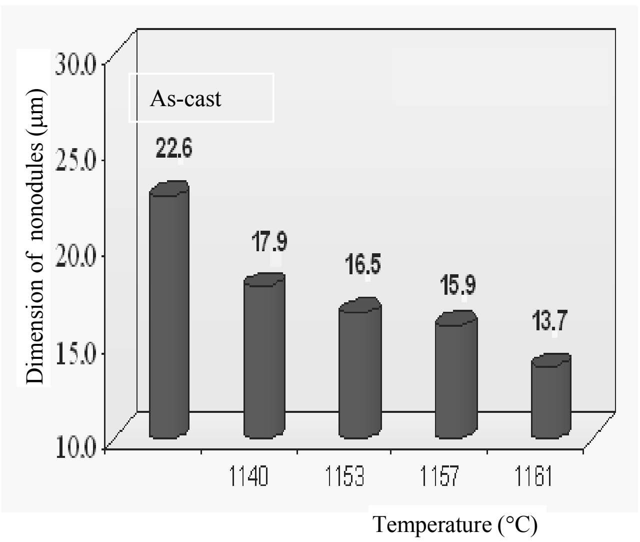


Fig. 10. Variation of dimensions of graphite nodules x thixocast temperature, for ASTM 536 nodular iron. (Holding time at the specific temperature: 30 min)

In addition, shorter heating cycle can prevent excessive growth of austenite grains, leading to finer solid in the semi-solid material. Previous studies have showed that finer globules in the thixotropic semi-solid can also be achieved if a previous deformation is imposed to the material, resulting in improved flow behavior [13]. Other studies bring additional information on the influence of previous deformation on austenite transformation and final grain size on ferrous alloys [14]. Moreover, to make it possible the prediction of heating conditions effects on structure transformations when producing a thixotropic semi-solid, the applicability of simulation methods already proved suitable for conventional heat treatment of steels [15] could be tested for the partial melting required to produce thixotropic material.

4. Conclusions

This work shows that, although presenting a wide solidification range, ASTM A536 nodular iron presents a narrow window of less than 28°C for semi-solid processing, which corresponds to the interval where eutectic transformation takes place and three phases coexist (austenite, graphite and liquid). At higher temperatures still within solidification range, the solid phase present (graphite) can dissolve in the liquid, what can lead to the deterioration of the material properties.

Moreover, in the range suggested for thixoforming, df_l / dT can be substantial, meaning that the liquid fraction in the semi-solid can change significantly with small changes in temperatures, demanding attention concerning the control of processing temperatures.

Thermodynamic calculations for temperature transformations must be taken with care; it must be remembered that practical conditions are far from equilibrium. Therefore calculated temperatures and liquid fraction sensitiveness can be significantly different from those present in practical conditions.

Semi-solid produced by partial melting shows globular solid phase (austenite) and liquid, a constitution that typically characterizes a thixotropic semi-solid.

Therefore, considering that a control of temperatures variation within 4 to 5°C is practically viable, thixoforming of ASTM A536 nodular iron, although requiring attention as far as temperature control is concerned, can be considered as feasible.

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