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Competitive Nucleation
in Grey Cast Irons

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Abstract

Cast irons are good examples of materials which are more sensitive to chemical composition and production conditions. In this research to improve casting quality, solidification and nucleation process in grey cast iron was investigate. In particular, attempts have been made to rationalize variation in eutectic cells with nucleation sites and eutectic solidification undercooling. Four castings with different diameter and similar chemical composition and pouring temperature and different inoculant percentage was casted. The cooling curve and maximum and minimum undercooling for each castings was measured. Also optical metallography and image analyzer has been used to determine the average eutectic cells diameter, and linear and surface densities, and volume density was calculated. The results of this research show a competitive behavior between nucleation sites and eutectic undercooling. Higher nucleation sites and higher eutectic undercooling cause higher eutectic cell density. But increasing nucleation sites by introducing inoculants to molten metal, is accompanied with reduction in eutectic undercooling. It means that inoculation and undercooling have opposite effect on each other. So, to achieve maximum cell density, it is necessary to create an optimization between these parameters.

Keywords: Cast iron, Nucleation, Undercooling, Cooling curve. Grain refining

1. Introduction

Cast irons are most important casting alloys. These alloys have many application in automotive, construction and machine building industries. This sensitivity is determined in part during solidification and in part during cooling transformations [1-2]. The phases formed during solidification of cast irons depend upon the casting and solidification procedure, the types and plenty of nucleation sites, amount of eutectic undercooling, chemical composition of the cast iron and so [1.3]. Figure 1 show microstructural evolution during the solidification of hypoeutectic grey cast iron. As shown, the solidification begins by precipitation of primary austenite from the melt, once the temperature falls below the liquidus temperature [4].

As the temperature decreases, the formation of dendrites causes the liquid to be enriched in carbon until the equilibrium eutectic temperature (Teut) is reached.

At this point, the eutectic composition is attained in the liquid and the nucleation of austenite - graphite eutectic cells can take place on or near dendrites. Further nucleation on sites within the melt and growth of existing nuclei ensues as more heat is extracted and the undercooling increases. Eventually, the latent heat released by solidification causes the temperature to rise. This reheating is called recalescence. The eutectic undercooling at the beginning of recallescence is called maximum undercooling.

After nucleation, the period of eutectic growth is begin, and a balance between the heat generated from eutectic growth and heat extracted from the mold is attained. The eutectic undercooling at this period is called minimum undercooling. At the end, the heat generated by solidification becomes smaller than the heat extracted from the mold and the solidification be complete.

Careful regulation of the melt chemistry and the use of proper inoculant is needed to control the formation of suitable type of graphite morphology [5].
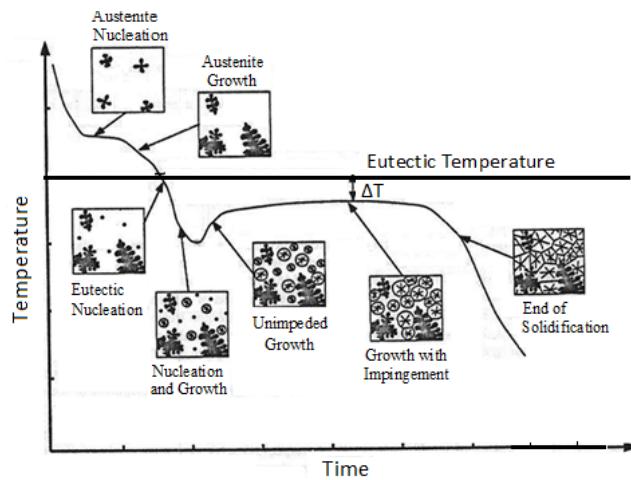

Fig. 1. Cooling curve and solidification microstructure of gray cast iron with hypoeutectic composition [4]

Sweden et.al [6] have shown that the use of an improper inoculant promotes flake graphite formation by:
– Raising the carbon equivalent of the melt
– Increasing the separation between the metastable Fe-Fe3C eutectic and the stable graphite eutectic temperatures.
– Providing additional nuclei in the melt.

But inoculation reduces the eutectic undercooling, which adversely effects the number of eutectic cells. The basic theory of heterogeneous nucleation has been outlined by Turnball and Fisher [7]. Hunt [8] shows that the nucleation rate at given undercooling is:

$$\frac{dN}{dt} = K_1(N_s - N)\exp(\frac{K_2}{(\Delta Tn)^2}) \tag{1}$$

Where:
Ns: Density of initial nucleation sites.
K_1: Collision frequency of the atom of the melt with nucleation sites of the heterogeneous particles.
K_2: Interfacial energy balance between the nucleus, the liquid and the foreign substrate on which nucleation occur.
ΔTn: Nucleation undercooling.

Figure 2 show the nucleation rate as a function of undercooling (ΔTn). In both cases, the nucleation even is approximately close to 0.5 seconds for ΔTn = 3 °C and 0.75 sec, for ΔTn = 10 °C. This short time nucleation lead to assuming that nucleation occurs instantaneously, therefore, when the nucleation undercooling (ΔTn) reaches the maximum undercooling nucleation occur instantaneously. In cast irons, nucleation may occur on a variety of components such as graphite, ferrosilicon, silicon dioxide, silicon carbide, calcium silicate, and such others. This type of nucleation may not be so far, and many investigations shown it [9-14]. As in equation 1, the nucleation rate may be affected by the density of nucleation sites, and

maximum undercooling that shall be investigated for its effects on the eutectic cell size.
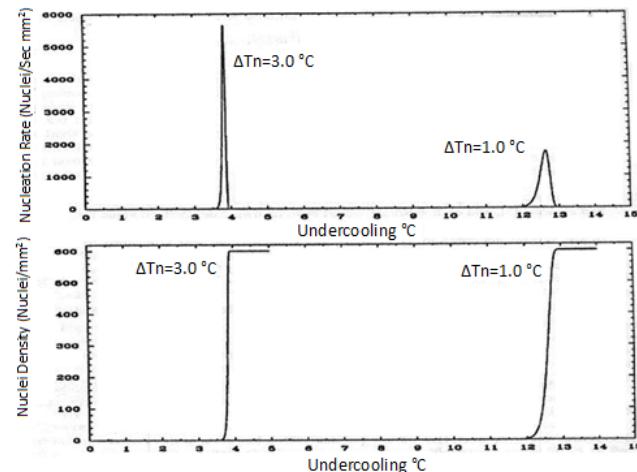

Fig. 2. Effect of undercooling on nucleation rate and cells density [4]

2. Experimental procedure

The following casting, figure 3, is used for experimental tests. Four cylindrical specimens with different diameters (15.7.19.1.25.3.33 mm) were cast to obtain different cooling rates. This casting was used by Oldfield, [13] and many other investigators [5-6, 15-16]. A sodium silicate bonded sand with AFS=70 was used as mold material. A type k thermocouple (Alumel - Chromel) with alumina sleeve and 4 mm diameter was located in center of each cylinder at approximately half second intervals.
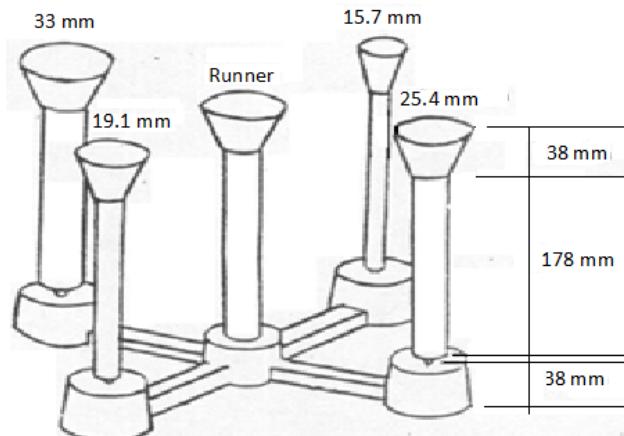

Fig. 3. Casting design and gating system [5-6, 15-16]

Three heats with approximate similar chemical composition were poured in the molds, and pouring temperature was approximately 1370 °C. Chemical composition of melts is shown in table 1. The first heat was not inoculated but the second, with 0.3 and the third with 0.5 weight percent supersede inoculated.

The chemical composition of inoculant is shown in table 2. For metallographic examination, the specimens were polished and etched with Steed reagent with following compositions.

> 10g cupric chloride (CuCl2)
> 200cc hydrochloric acid (HCl)
> 1000 cc of ethyl alcohol
> 40 g magnesium chloride (MgCl2)

Table 1.
Chemical composition of melt and inoculation (wt. %)

Heat	%C	%Si	%S	%P	%Mn	%CE	Ino.wt.%
1	3.3	2.1	0.08	0.07	0.58	4.1	0
2	3.45	2.01	0.085	0.08	0.54	4.12	0.3
3	3.38	2.2	0.08	0.08	0.56	4.11	0.5

Table 1.
Chemical composition of melt and inoculation (wt. %)

% Si	%Ca	% Sr	% Fe
73-78	0.1 Max	0.6-1	Remand

The salts were dissolved in about 5mililiter of hot water and then the alcohol was added and the specimens were immersed in solution for 2.5 hours. Average diameter, Liner density (N_L) and surface density (N_A) of cells were determined by an image analyzer. Volumetric cells density is calculated from equation.2 [17].

$$N_v = 0.5659\,(N_L)^2 \tag{2}$$

There are many equations to determine eutectic temperature but, one presented by Glover [18] correlated best with the experimental results.

$$T_{eut}\,(°C) = 1135.06 + 13.98\%Si - 2.05\%Si^2 \tag{3}$$

3. Discussion

The resulting cooling curves and eutectic cells structures from 19.1 mm diameter castings are shown in fig. 4 and 5 respectively. The resulting data are presented in Table 3. It is reported, by increasing eutectic undercooling, the cells density increases and the average cells diameter decrease. By referring to table 3, the similar results can be observed. Increase in casting diameter, decrease eutectic undercooling and cells density decreases.

Furthermore, by increasing nucleation sites.it is reported that cells density increases, but this is not seen in the castings. Nucleation agent (inoculant) increases nucleation sites but decreases eutectic undercooling, hence there is competitive reaction between nucleation sites and eutectic undercooling. Resulting data are presented in table 3 show that, in castings with 0.3% inoculant the eutectic cell density is higher than 0.0% and 0.5% inoculant. In 0.0% inoculant casting, the eutectic undercooling is higher than 0.3% and 0.5% but without inoculant material, the nucleation sites is less. In castings with 0.3% inoculant, inoculation sites are higher and the cells density is maximum.
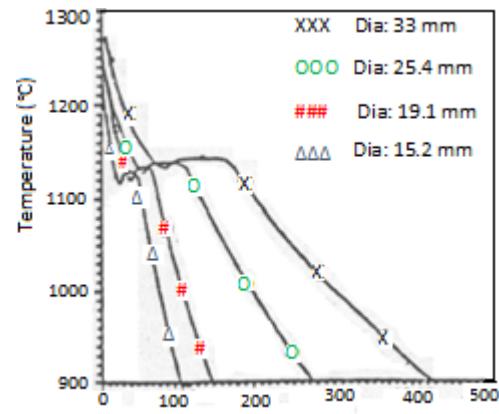

a)
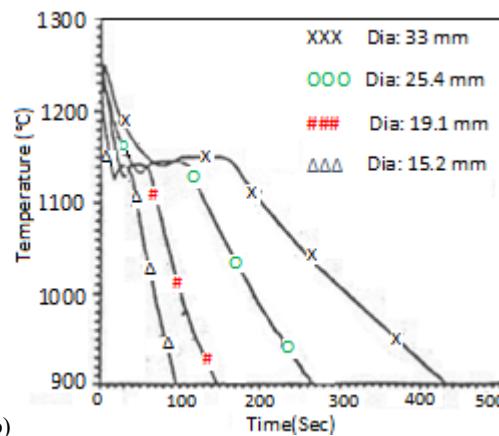
b)
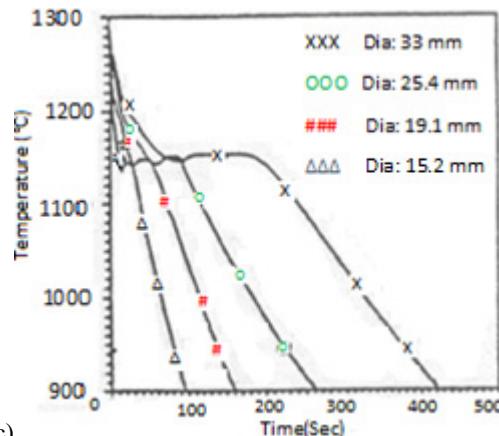
(c)

Fig. 4. Cooling curve of 19.1 mm diameter castings
a) 0.0% inoculant, b) 0.3% inoculant, c) 0.5% inoculant
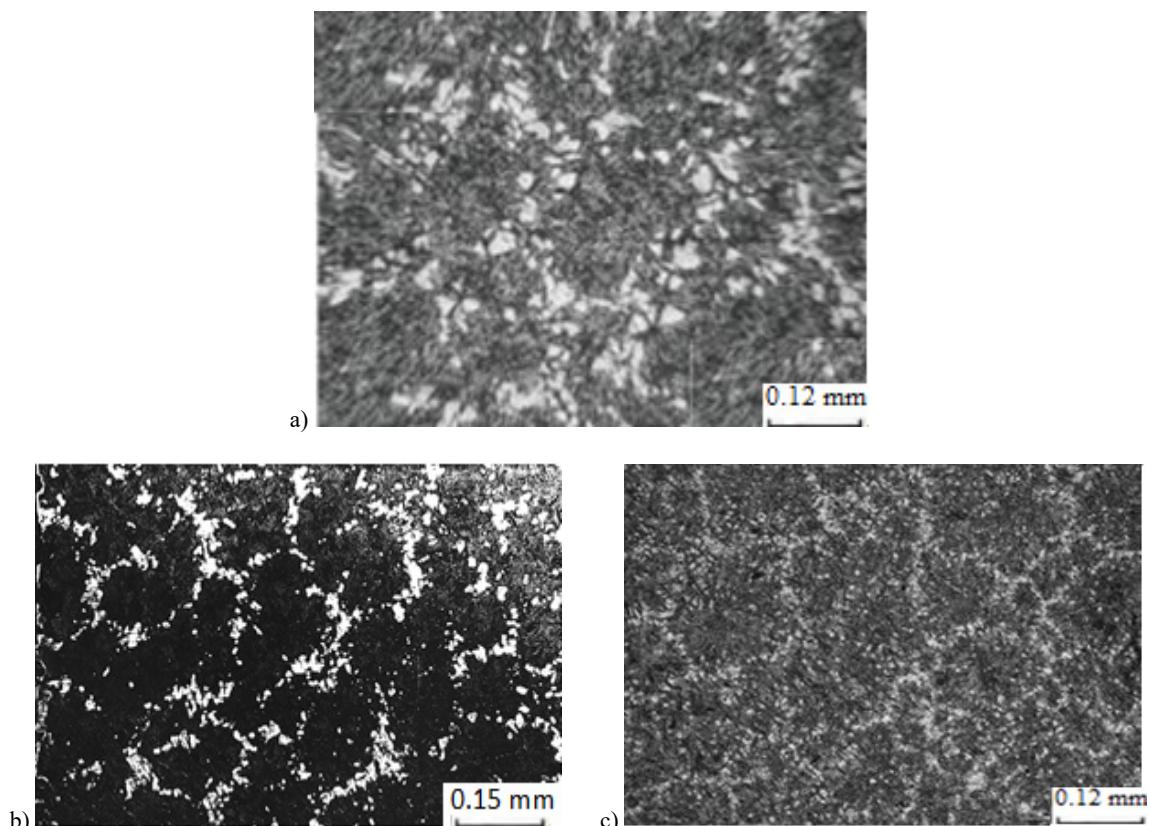
Fig. 5. Eutectic cells images from castings with 19.1 mm diameter
a) 0.0 wt.% inoculant, b) 0.3 wt. % inoculant, c) 0.5 wt.% inoculant

Table 3.
Resulting data from casting samples

Castings dia. (mm)	Eutectic Temp. °C	Maximum undercooling °C	Minimum undercooling °C	Inoculant wt.%	Average cell dia. (mm)	Cell Density Cells/cm^2	Cell Density Cells/mm^2
15.7	1153.5	23	38	0.0	0.694	376	5.72
15.7	1156.3	15	31	0.3	0.41	1079	27.58
15.7	1156.5	11	22	0.5	0.432	978	23.82
19.1	1153.5	19	33	0.0	0.862	243	2.98
19.1	1156.3	13	28	0.3	0.43	986	24.11
19.1	1156.5	8	15	0.5	0.542	619	12.03
25.4	1156.5	14	25	0.0	0.942	203	2.28
25.4	1156.3	10	23	0.3	0.444	912	21.46
25.4	1156.5	6	13	0.5	0.62	472	8.03
33	1153.5	10	20	0.0	1.244	116	0.99
33	1156.3	6	15	0.3	0.588	527	9.46
33	1156.5	4	10	0.5	0.744	327	4.64

In castings with 0.5% inoculant, the nucleation sites are high, but eutectic undercooling is reduced. Therefore the cells density is lower. As seen, there is a competing behavior between nucleation sites and eutectic undercooling. To increase cells density, it is necessary to create an optimization between nucleation sites and eutectic undercooling. As a result, it can be seen that, with 0.3% inoculant agent, the cells density is maximum.

4. Conclusion

1. Addition of inoculant to molten cast iron, increase eutectic cells density.
2. Increase of eutectic undercooling, cause the eutectic cells increasing.
3. Increase eutectic undercooling, increase the nucleation sites and resulting increase eutectic cells density.

4. In high eutectic undercooling and less nucleation sites, or, less eutectic undercooling and high nucleation sites, the cells density is not maximum.

5. An optimization must be create between nucleation sites and eutectic undercooling to maximize eutectic cells density.

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