A RESEARCH ON THE CALCULATION OF GRAPHITIZATION ABILITY OF GRAY CAST IRONS

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Abstract: *In this research the relationship between graphitization ability and the carbon equivalent (CE %) of a cast iron have been investigated. The first series of moulds were cast at CE of 3.2% and pouring temperature of 1350°C. The other moulds were cast at different CE% with varying Si content. The graphitization ability(π_c) was calculated using the thermodynamics aspects of graphitization and CE%. The results showed that the graphitization ability increases with an increase in CE% and decrease with pouring temperature.*

Keywords: *Graphitization ability, Carbon activity in molten cast iron, carbon equivalent*

1. INTRODUCTION

The ability of a cast iron alloy to the graphite phase formation is called the graphitization [1]. As the graphitization ability of the cast iron increases, the melting point temperature and solidification shrinkage decrease and the fluidity increase. Ability of vibration absorption, thermal conductivity and machining Capability also increase [2].

In order to measure the cast iron alloys tendency to graphitization, the carbon potential $\pi_c = RTLn\ a_c$ (a_c is the thermodynamic activity of carbon) should be calculated. When $\pi_c > 0$ the alloy tends to graphitization (although, for kinetic reasons, under real conditions it may solidify as white); when $\pi_c < 0$ the alloy is white and stable, and graphitization is not possible. Graphite was taken as the standard state i.e. $\pi^{gr}_c = 0$ and $a^{gr}_c = 1$[1, 3].

The effect of alloying elements on the graphitization potential of cast iron was investigated by A. A. Zhukov. As seen in Fig.1 the graphitization potential has been increased as the silicon content increased. This has been attributed to reduction of carbon solubility in austenite phase so that carbon diffuses outward and converts to graphite. It should be also attributed to very low solubility of Si in carbide which in turn prevents carbide formation [3].

In Fe-C-Si systems, silicon plays the role of a valent-element donor. The behaviors of silicon and carbon atoms in the vicinity of iron atoms are similar. They have similar homologic configurations in the valent layers: $1S^2\ 2S^2\ 2P$ for C and $1S^2\ 2S^2\ 2P\ 3S^2\ 3P^2$ for Si. Four sp-valent electrons can be accepted by the iron atoms in liquid or solid solutions of Fe-Si-C. The carbon atoms are completely ionized $C \longrightarrow C^{4+} + 4e^-$ in the solid solutions, while the degree of ionization is slightly lower than four in the liquid solutions, although it is sufficiently high [4].
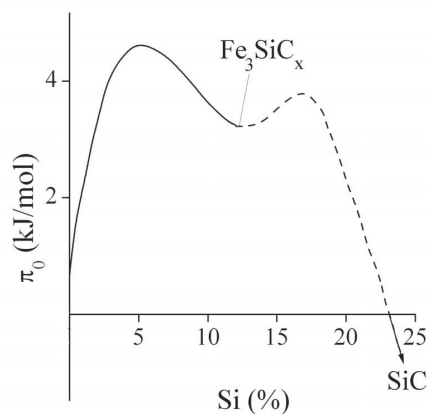

Fig. 1. Effect of Si content on the tendency of cast iron to graphitization [2].

Silicon is a more generous donor than carbon, since its 3sp-valent electrons are further from the nucleus than the 2sp-valent electrons of the carbon, and, moreover, are shielded by two interlayer layers, whereas for carbon, there is only one shielding layer containing a total of two electrons. Consequently, the ionization potential of silicon is lower than that of carbon. As a result, the silicon metal is always in a more suitable position than the carbon metalloid in its competitive struggle for chemical bonding with the surrounding iron atoms.

Where Si atoms in iron-base liquid and solid solutions occupy lattice nodes in place of Fe atoms (substitutional solutions), and C atoms occupy the internodes (interstitial solutions), the "entry" to certain zones surrounding each Si atom should be prohibited by interstitial atoms in this case. This increases the actual concentration of the interstitial [4, 5].

The addition of silicon to a binary iron-carbon alloy decreases the stability of Fe_3C, which is already metastable, and increases the stability of graphite and eutectic and eutectoid transformation temperatures [6].

In the iron-graphite system some alloying elements such as copper, aluminum and nickel have a similar behavior to silicon and increase the eutectic transformation temperature but some of them such as manganese and phosphorus decrease it [7,8].

The susceptibility of iron-carbon alloys to graphitization can be evaluated from their phase diagrams by the distance between the lines of metastable (m) and stable (s) equilibriums "along the horizontal" (i.e. along the isotherms)

The eutectic transformation temperatures in the (Fe -G) and (Fe –Fe_3C) systems for the various alloys can be calculated using Table 1 and eq.1 and 2[6].

$$T_{st}=1154(°C) + wt\%Si \times C'_{Si} + wt\%Cu \times C'_{Cu} + wt\%Al \times C'_{Al} +...$$
(1)

$$T_{met}=1148(°C) + wt\%Si \times C_{Si} + wt\%Cu \times C_{Cu} + wt\%Al \times C_{Al} +...$$
(2)

Where T_{st} and T_{met} are eutectic transformation temperatures (°C) in the Fe-G (stable) and Fe-Fe_3C (metastable) systems after considering the effect of alloying elements, respectively; wt% is the weight percent of elements; C and C´ are the coefficients related to the eutectic temperature variations in Fe-G and Fe-Fe_3C systems according to the weight percentage of elements, respectively; 1154 °C and 1148 °C are the eutectic transformation temperatures of Fe-G and Fe-Fe_3C systems respectively when no alloying elements are added [6].

Table 1. Equilibrium partition coefficients of a third element X in the Fe-C-X system [5].

Element	Eutectic, °C/wt%X	
	Metastable C	Stable C´
Silicon	-10 to 20	4
Copper	-2.3	5
Aluminum	-1.5	8
Chromium	7	-
Manganese	3	-2

Table 2. Si and C content and CE% of samples cast at different conditions

Sample	wt% C	wt% Si	CE%	X_c	X_{Si}
1	2.521	1.698	3.087	0.106	0.03
2	2.519	2.114	3.223	0.106	0.038
3	2.518	2.873	3.475	0.105	0.051
4	2.517	3.748	3.766	0.104	0.066
5	2.515	4.012	3.852	0.104	0.071
6	2.516	4.373	3.973	0.103	0.077
7	2.514	4.603	4.048	0.103	0.081
8	2.513	4.961	4.166	0.103	0.087

2. EXPERIMENTAL PROCEDURE

The pattern that was used for molding is shown in Fig. 2. Melts with different silicon contents (Table 2) were produced in an induction furnace. The first series of mould were cast at CE of 3.2% and pouring temperature of 1350˚C. The other moulds were cast at the same temperature with different CE% by varying the Si content. With considering the thermodynamic equations and chemical composition of the specimens, carbon activity and numerical content of π_c were calculated at 1600 ˚C, 1350 ˚C (casting temperature) and eutectic transformation temperature, for all specimens. The samples were cut and the volume fraction of graphite was measured in different parts of cross-sections by Clemex Image Analysis software, version 3.5.
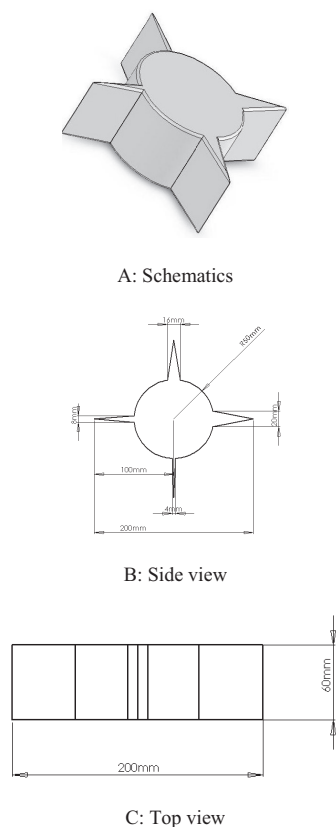
3. RESULTS AND DISCUSSION

3. 1. Calculation of Differences Between Stable and Metastable Eutectic Transformation Temperatures:

Table 2 shows the Si and C content and CE% of the samples. Using equations 1 and 2, and calculating the differences between stable and metastable eutectic transformations temperature ($\Delta T = T_{st} - T_{met}$), graphitization potential ability can be exhibited.

Table 3 illustrates the stable and metastable eutectic temperatures for different alloys. As shown, the above mentioned temperatures will increase from 37 to 100 ˚C as the Si content increase. This is equivalent to graphitization ability enhancement, because Fe-G transformation is done in an extended range.

3. 2. Carbon Activity Calculation of the Molten Metal:

Carbon activity in the molten Fe-C-Si state, is its activity for graphitization and can be calculated using equation 3. That is carbons ability for realizing the graphite phase, and is not solving activity. That is the carbons ability for being solved [6].

A: Schematics

B: Side view

C: Top view

Fig. 2. Geometry of pattern

Table. 3. Eutectic transformation temperatures of (Fe-Fe₃C) and (Fe- G) systems for different samples

sample	T(st)	T(met)	ΔT
1	1159.9	1122.1	37.8
2	1161.7	1116.1	45.6
3	1164.4	1104.2	60.2
4	1168.1	1091.1	77.0
5	1169.1	1087.2	81.9
6	1170.9	1081.2	89.7
7	1171.7	1077.6	94.1
8	1173.1	1072.5	100.6

$$Log\ a_C = \frac{1180}{T} - 0.87 + (\frac{2540}{T} + 3.84)X_C - (\frac{1270}{T} + 1.74)X_C^2 +$$

$$+ LogX_C + (\frac{1423}{T} + 4.75)X_{Si} - (\frac{153}{T} + 3.02)X_{Si}^2 - (\frac{1423}{T} +$$

$$4.76)X_C X_{Si} \tag{3}$$

In this equation, X is the elements content, T is temperature (K) and α_c is the carbon's activity in compare with the standard state (Raoult's activity). By use of equation 3, Raoult's activity of carbon can be calculated in each temperature.

Obviously activity means the weight percent and hence Raoult's activity in the calculation of chemical potential weight percent activity must be replaced.

Therefore, at the first by of carbon, Henry's activity and then weight percent activity should be calculated.

For Henry's activity, at the first, coefficient of Henry's activity must be calculated. For this reason, equation 4 is used [6]:

$$Log\frac{\gamma_C}{\gamma_C^o} = -2\alpha_{Fe-C}X_C + (\alpha_{C-Si} - \alpha_{Fe-C} - \alpha_{Fe-Si})X_{Si} + \alpha_{Fe-C}X_C^2$$

$$+ \alpha_{Fe-Si}X_{Si}^2 + (\alpha_{Fe-C} + \alpha_{Fe-Si} - \alpha_{C-Si})X_C X_{Si}$$

$$\tag{4}$$

Where γ_C and $\gamma^\circ c$ are coefficients of Raoult's and Henry's activity respectively, α is a coefficient of temperature function and X is the weight percent of elements. α_{Fe-C} and α_{Fe-Si} can be determined by equations 5 and 6 consequently. Also, equation 7 is used for calculation of α_{C-Si}[6].

$$\alpha_{Fe-c} = -\left(\frac{1270}{T} + 1.74\right) \tag{5}$$

$$\alpha_{Fe-Si} = -\left(\frac{153}{T} + 3.02\right) \tag{6}$$

$$\frac{\varepsilon_{C-Si}}{2.303} = \frac{\varepsilon_{Si-C}}{2.303} = \alpha_{C-Si} - \alpha_{Fe-C} - \alpha_{Fe-Si} \tag{7}$$

Where ε_{C-Si} is a factor for exhibition of Si effect on carbon that is determined by equation 8[6].

$$\varepsilon_{C-Si} \times X_{Si} = 2.303 \times e_{C-Si} \times wt\%Si \tag{8}$$

In equation 8, e_{C-Si} is a coefficient for exhibition of the effect of Si on carbon that can be determined using thermodynamic tables. This value (e_{C-Si}) is 0.08 for 1600 °C and can be used as an approximate value for other temperatures.

After calculating the $^\circ\gamma_C\gamma/_C$, γ_C using equation 7, the $\gamma\ ^\circ_C$ can be calculated for each alloy at 1873 K, 1623 K and eutectic temperature [6].

$$\gamma = \frac{a_C(R)}{X_C} \tag{9}$$

By determination the coefficient of Henry's activity of carbon ($\gamma^\circ c$), using equation 10, Henry's activity value will be calculated as follows[6];

$$a_C(H) = \gamma_C^\circ \times X_C \tag{10}$$

The weight percent activity is calculated by equation 11[5].

$$a(wt\%) = a(H) \times \frac{100 \times MW_C}{MW_{Fe}} \tag{11}$$

3. 3. Calculation of Graphitization Potential

By calculating the activity of weight percent and using equation 12, graphitization potential of molten state can be shown as [6];

$$\pi_C = RT\ Ln(a_C(wt\%)) \tag{12}$$

Calculated value of Raoult's activity, Henry's activity and activity of weight percent, and the melting potential for graphitization (π_c) at 1873, 1623 K and eutectic temperature of Fe-C transformation are given in Tables 4, 5 and 6.

Fig. 3 illustrates the π_c values as a function of silicon content in the mentioned temperatures.

As can be seen, the graphitization potential of the melt at a constant temperature increases with increasing Si content. This is because, silicon reduces carbon activity in the austenitic state then decarburizing occurs and carbon goes out of austenite phase.

Decarburizing increases the carbon's vapor pressure upon the system and carbon's activity in solution and ultimately increases the graphite volume fraction of the microstructure. As the

Fig. 3. Effect of silicon percent on the graphitization potential in 1873 K, 1623 K and eutectic transformation temperatures in (Fe- G) system of alloys

Table. 5. Calculated results of Raoult, Henry and weight percent activities and graphitization potential at 1623 K

sample	a_R	a_H	$a_{wt\%}$	π_C
1	0.349	0.096	1.513	5.594
2	0.377	0.102	1.599	6.337
3	0.431	0.112	1.757	7.607
4	0.497	0.124	1.949	9.011
5	0.527	0.130	2.033	9.579
6	0.547	0.134	2.094	9.973
7	0.568	0.137	2.153	10.351
8	0.601	0.143	2.245	10.917

temperature decreases, the amount of graphite increases to the highest value that can be obtained at eutectic temperature. The graphitization potential at 1873 K increases from 2.8 to 8.7 KJ/mol. The same value increase from 5.5 to 10.9 at 1623 K and from 7.6 to 12.42 KJ/mol at eutectic transformation temperature of Fe-C.

A reason for computation of informations at 1600 ˚C is the thermodynamical data that are given at the mentioned temperature. This temperature also used for the comparison between π_c values at different temperatures.

A comparison between the calculated results of graphitization potential (Fig.3) and Zhukov's results (Fig.1) shows that both of them are corresponding to each other. By attention to these

figures, the graphitization potential increases linearly with Si content up to 5%. Zhukov didn't mention the experiment temperature and calculation methods. By the way, determined results at 1873K are nearer to these results.

Figures 4.A and 4.B show the optical microstructure of the specimen with 3.85% and

Table. 4. Calculated results of Raoult, Henry and weight percent activities and graphitization potential at 1873 K

sample	a_R	a_H	$a_{wt\%}$	π_C
1	0.264	0.076	1.201	2.861
2	0.285	0.081	1.267	3.690
3	0.324	0.088	1.388	5.106
4	0.373	0.098	1.534	6.669
5	0.395	0.102	1.598	7.306
6	0.410	0.105	1.643	7.739
7	0.426	0.108	1.688	8.161
8	0.449	0.112	1.758	8.790

**Table. 6.** Calculated results of Raoult, Henry and weight percent activities and graphitization potential at eutectic transformation temperature in (Fe- G) system of different samples

sample	a_R	a_H	$a_{wt\%}$	π_C
1	0.461	0.121	1.904	7.672
2	0.498	0.128	2.011	8.330
3	0.567	0.141	2.207	9.463
4	0.652	0.156	2.445	10.716
5	0.691	0.163	2.550	11.224
6	0.716	0.167	2.622	11.572
7	0.743	0.172	2.696	11.913
8	0.786	0.179	2.810	12.422

A: CE= 3.852%   B: CE= 4.166%
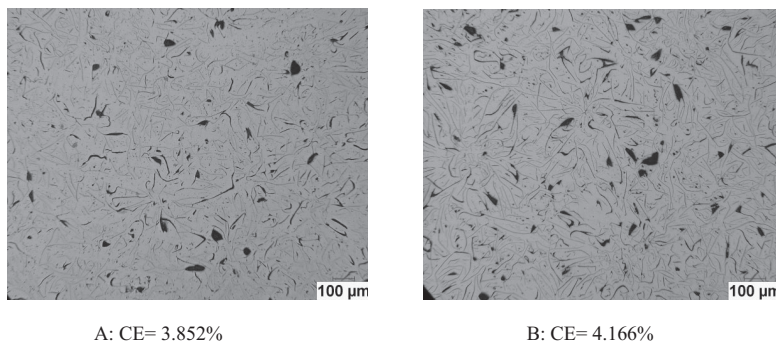
Fig. 4. Microstructures of specimen at different CE%

4.16% carbon equivalent respectively. It can be seen that the graphite content increases in Figure 4.B due to increasing of the carbon equivalent content. By using Clemex Image Analysis software, it is calculated that the volume fraction increases from 12.87% in Figure 4.A to 17.56% in Figure 4.B.

4. CONCLUSIONS

The following conclusions can be made from this work;
1. As the Si content increases the eutectic transformation temperature of Fe-C increases and eutectic transformation temperature of Fe-Fe3C decreases. The differences between these two temperatures can be inferred as a criterion for graphitization ability.
2. With calculation of π_c and carbon's activity in the melt, the graphitization ability of the melt, can be calculated and volume percent of graphite can be predicated.
3. Melting potential for graphitization increases with increasing the carbon equivalent at the constant temperature.
4. By temperature reduction, melting potential for graphitization has increased. The highest value has been obtained at eutectic temperature.
5. Graphitization potential of melt increases from 7.6 to 12.42 Kj/mol at eutectic transformation temperature of Fe-C system.

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