Effect of Si Segregation on Low Temperature Toughness of Ductile Iron

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ABSTRACT

Microstructural features as graphite morphology and element segregation in ductile iron are originated during solidification. These phenomena significantly affect impact toughness and the ductile-to-brittle transition temperature (DBTT) of ductile iron, limiting low temperature applications. Room/low temperature tested Charpy specimens with a wide range of nodule count were taken from different locations in a 10 in. diameter continuously cast bar and the heavy section of no-bake sand castings. In the as cast condition, regular composition ductile iron (2.5% Si) with finer graphite structure exhibits higher toughness when compared to ductile iron with large graphite. On the contrary, in silicon homogenized ductile iron, significant increase in impact toughness and decrease of DBTT were observed in specimens with larger graphite nodules and neighboring nodule distances. To mitigate the negative effect of Si segregation in a heavy section, ductile iron casting with 1.5% Si was produced and tested at different temperatures. The results showed the possibility of significantly decreasing the DBTT temperature below -40°C (-40°F) and increasing impact toughness. Thermodynamic analysis and diffusion modeling solidification segregation together with first principle calculations of shear and cleavage of Body Centered Cubic (BCC) Fe alloyed with Si were used to understand the brittleness phenomena and can be applied for alloy design.

Keywords: ductile iron, low temperature toughness, segregation, diffusion

INTRODUCTION

Silicon is the third (after iron and carbon) main component in cast iron. Si increases the thermodynamic activity of C in liquid Fe-C-Si alloys, promoting formation of a stable graphite-austenite eutectic and decreasing the tendency to form cementite (chill). The shape of graphite phase also affects the chilling tendency in a solidified casting. Flake graphite grows in direct contact with the liquid phase when carbon atoms have a high mobility. Growth of spherical graphite is limited by slower carbon diffusion through a surrounding austenite shell. To avoid the formation of eutectic cementite, ductile iron with spherical graphite has to have a higher level of silicon than comparable gray iron with flake graphite.

The second most important role of Si in ductile iron relates to the promotion of eutectoid ferrite formation from decomposed austenite by increasing C activity and diffusivity in austenite. Having a higher toughness and ductility at room temperature, ferritic iron with spherical graphite is an appropriate candidate for many transportation applications. During the last decade, growing interest in economical strong cast materials for low temperature applications has been observed for such areas as wind energy and offshore drilling systems.

Unfortunately, high Si reduces the low temperature toughness of iron alloys with a ferrite matrix. The first consideration led us to review the effect of Si alloying on the mechanical properties of ferritic steel to exclude the effect of graphite phases. For example, low carbon high silicon steels (up to 6.5% Si) are widely used as soft magnetic materials in transformers, motors and power generators. However, when the Si content increases the material becomes brittle and is difficult to work using conventional hot and cold rolling processes. The toughness of BCC Fe alloyed with Si was studied by Srinivas et al. Silicon additions markedly increased the strength and decreased the tensile ductility as well as the work hardening exponent of ferrite. Silicon leads to cleavage instability during monotonic loading. Fracture toughness $J_{lc}$ decreased from 140 kJ/m$^2$ in pure BCC Fe to 97 kJ/m$^2$ and 42 kJ/m$^2$ when alloyed with 0.5% Si and 2.5% Si, respectively.

Crack initiation in ductile BCC Fe involves the development of: (i) a plastic zone ahead of the crack tip, (ii) void nucleation and (iii) growth and coalescence within a plastic zone. The fracture toughness $J_{lc}$ is proportional to the energy expended in all three of these processes. On the other hand, cleavage fracture occurs in Si-alloyed Fe-BCC when its resistance to slip is so high that the cohesive strength is reached locally before the resistance to slip is overcome. In Si-alloyed ferrite, plastic zone size is restricted by a higher strength and lower work hardening exponent, which leads to higher stress concentration ahead of the crack tip. Cleavage fracture with less spent energy occurs when the local stress concentration exceeds a critical value of stress.

When there is a spherical graphite phase present in the ferrite matrix, silicon has an even more destructive effect
on ductility and toughness of as cast ductile iron\(^3,4\) when compared to steel. The principle reason for this is the Si rejection during solidification, which increases the local Si concentration around the graphite nodules.\(^5\) Negative Si segregation around nodule graphite is another factor lowering the impact toughness of ductile iron, because the boundary between graphite nodules and the ferrite matrix is a place where cracks are initiated.

According to the Fe-Si phase diagram, the intermetallic phases B2 (Fe\(_2\)Si) and D03 (Fe\(_3\)Si) can be formed when ferrite is alloyed with more than 4.5% Si. The lack of low-temperature ductility in less Si-alloyed ferrite can be attributed to structural ordering of Si atoms in the BCC lattice. In a simplified explanation, the Si behavior can be related to the atomic misfit parameters—Si with a smaller atomic size contracts the BCC lattice and produces a disproportional amount of strengthening from a relatively small misfit. Combined (X-ray, ultraviolet, photoelectron, Auger-electron) and other methods showed the bonded state of Si atoms as segregated superstructures in a BCC lattice.\(^6\) The near Fermi energy, \(E_c\), electron density is always high, reflecting the intermetallic character of the Fe-Si compounds. It was shown that at room temperature the Si-Si cluster interactions are more attractive when compared to Fe-Si interactions. When comparing the effects of Si to Ni, both alloying elements increased the room temperature yield stress of single-crystal BCC Fe while softening (decrease strength) ferrite at a low temperature. At the same time, Ni drastically decreased the DBTT of pure BCC Fe while Si increased the DBTT to above room temperature.

In an attempt to understand the microstructural and atomic mechanisms of brittleness and increasing DBTT in Si-alloyed BCC Fe, molecular dynamic (MD) and first principle atomic modeling were performed and compared to experimental data.\(^6,11\) The simulated pure BCC Fe crystal has the same orientation and similar geometry as in the fracture experiments. The edge crack lies on a (001) plane, the crack front is oriented along the [110] direction and the direction of potential crack extension is [-110]. Silicon alloying can change the preferable crack direction. The critical value (1.75) of the ratio of bulk modulus (B) to shear modulus (G) at absolute zero temperature was used to predict the effect of alloying elements (Al, Si, V, Cr, Mn, Co, Ni, Rh) in BCC Fe on the ductile to brittle transition.\(^12\) All of the additions were found to decrease the B/G ratio, meaning that they increase the brittleness, which is not always supported by experimental data for these alloying elements. More experimental studies combined with thermodynamic, diffusion and ab-initio atomic calculations must be done to understand the phenomena of the dramatic decrease of low temperature toughness of Si alloyed ductile iron.

The objective of this study was to understand the effect of Si segregation on low temperature impact toughness of ductile iron using experimental and modeling techniques.

**PROCEDURES**

**EXPERIMENTAL**

Charpy impact tests were performed at room and low temperatures (down to -60°C [-76]) using two types of ductile iron. The first one was industrial continuously cast mostly ferrite/pearlite ductile iron with composition shown in Table 1. The reason for choosing continuously cast ductile iron was the wide spectrum of graphite nodule counts in different locations of 10 in. diameter bars solidified with a large thermal gradient in a water-cooled graphite mold. Samples were cut in the longitudinal direction at different distances from the cast surface. The second ductile had less silicon and was produced at MS and T laboratory (Table 1). Specimens of this ductile iron were cut from heavy 4 in. × 10 in. × 10 in. cast block solidified in no-bake sand molds. This particular composition of ductile iron was chosen for decreasing Si-segregation in heavy sections of castings. The melt was prepared in a 200-lb induction furnace from pure induction iron and Sorel metal, pre-treated by 0.04% Ce mishmetal, and treated in the ladle by 1.7% Fe-50% Si-5% Mg spheroidizer with 0.6% Fe-70% Si-2% Ba inoculant. Ductile irons were tested in as cast condition and after homogenization heat treatment, parameters of which will be described. The graphite structure and fractured surfaces were studied with an automated (Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX) ASPEX system. A special algorithm was developed for counting neighboring graphite nodule distances based on X and Y coordinates of the center of each graphite nodule.

**THERMODYNAMIC AND DIFFUSION MODELING**

The element segregation which originated during solidification was modeled using FACTSAGE thermodynamic software and followed “natural” diffusion homogenization during casting cooling was modeled using FLUENT computational fluid dynamic (CFD) software. Thermodynamic equilibrium in the mushy zone between graphite, austenite and the remained melt was calculated based on free energy minimization of all phases while taking into consideration the mutual effect of elements on its activity. FSTEEL, FMELT, FFCC, and ELEMENT data bases were used. A concentration of

| Table 1. Chemical Compositions (wt. %) of Studied Ductile Iron |
|-----------------|---|---|---|---|---|---|---|---|
| **Iron**        | **C** | **Si** | **Mn** | **Cu** | **Cr** | **S** | **P** | **Mg** | **Ce** |
| **Continuous**  | 3.6 | 2.5 | 0.3 | 0.04 | 0.03 | 0.01 | 0.01 | 0.045 | -     |
| **Sand mold**   | 3.9 | 1.5 | 0.1 | 0.03 | 0.03 | 0.01 | 0.01 | 0.034 | 0.02  |
elements in solidified layers of austenite around spherical graphite were step by step recalculated from equilibrium using the Scheil approach, assuming zero diffusivity in the solid and full homogenization of the remaining liquid. This approach can be used as an extreme case, which provides the maximum possible segregation developed during solidification.

In heavy section, the cooling rate significantly slowed down after casting solidification. During slow cooling, some diffusion homogenization could have taken place. To analyze this “natural” diffusion homogenization, the transient Transport and Reaction module of FLUENT was applied to the meshed individual three dimensional spherical cell containing a graphite nodule surrounded by metal matrix. Geometric representation of the real ductile iron structure was done using known quantitative stereology correlations between three- and two-dimensional structure parameters. Element segregation that occurred during solidification was determined from thermodynamic calculations and introduced into the shell by applying special “patching” procedures (Fig.1). Non-steady state modeling was used to solve diffusion homogenization during casting cooling at a particular cooling rate. A multicomponent dilute model, in which the diffusion mobility of element, \( i \), does not depend on concentration of element, \( j \), was used. The experimental values of diffusivity and activation energy of Si and Mn in FCC Fe were taken from the literature. The same approach was also used to model diffusion during isothermal heat treatment.

**AB-INITIO ATOMIC MODELING**

Ab-initio calculations were performed to determine the silicon alloying effect on the structural, electronic and magnetic properties as well as the deformation behavior of BCC Fe. The projector-augmented waves (PAW) method, as implemented in the Vienna ab initio simulation package (VASP), was used with the generalized gradient approximation (GGA) for the exchange-correlation energy. The fracture and deformation behavior in the alloy was analyzed using the Rice-Thompson criterion, where the brittle-ductile behavior is analyzed by the comparison of two competitive processes: the crack opening (brittle fracture) and the emission of a dislocation near the crack tip (plastic deformation).

Two energy characteristics were calculated with first-principle methods to describe these processes quantitatively: (i) the cleavage energy \( G_c \), which models the crack and (ii) the unstable stacking fault energy \( G_{SF} \), which represents the maximum energy for sliding of atomic planes and simulates the lattice resistance to dislocation emission. \( G_c \) was calculated as the required energy for splitting of a crystal into two semi-infinite parts (i.e., \( G_c \) is energy required for creating of two surfaces \( G_c = 2\gamma_s \) where \( \gamma_s \) is surface energy). The energy of a generalized stacking fault defect \( G_{SF} \) was modeled by the total energy change caused by a rigid shift of a half of crystal along a direction in the slip plane. The (001) plane was considered for both cleavage and sliding. The goal was to give the qualitative prediction of the effect of silicon on brittle/ductile behavior.

**RESULTS**

**PREDICTION OF SEGREGATIONS IN DUCTILE IRON**

The effects of alloying elements on the thermodynamic activity of components in liquid (melt) and solid (austenite) solutions are the main driving force of segregation originating in the cast structure. The real final picture also depends on such kinetics factors as transformation time (cooling rate), diffusion distances (heterogeneous nuclei density) and diffusivity. Calculation of thermodynamic driving forces for element redistribution can predict maximal possible scenario. Such calculated negative Si-segregation (elevated Si concentration near graphite) and positive Mn-segregation (increased Mn concentration in the last solidified interdendritic region) are illustrated in Fig. 1. These segregations originated during solidification of the spherical graphite–austenite eutectic. In ductile iron with average 2.5% Si content, layers near a graphite nodule could theoretically have up to 4% Si, linearly decreasing toward a eutectic cell boundary (Fig. 2). On the contrary, Mn segregation was accelerated at the end of solidification.

\[ \text{Fig. 1. The model shows (a) negative Si and (b) positive Mn) segregations in austenite shell surrounded spherical graphite that originated during solidification.} \]
Fig. 2. The graph shows the calculated segregation of Si and Mn during ductile iron solidification (Scheil model, FACTSAGE).

Two factors promoted a partial “natural” structure homogenization during cooling casting in the sand mold. The first one is a rapid decrease of cooling rate after casting solidification in sand mold. The second factor is related to a high diffusion mobility of alloying elements near the melting point. Illustrations of the initial (as solidified) segregation and that after partial “natural” homogenization during cooling of a heavy section casting with 0.1°C (34°F)/sec (as cast) are given in Fig. 3. These diffusion calculations were performed for a spherical eutectic cell with 50 µm diameter. The calculated segregations in as cast condition were still significant, while substantially less than what originated during solidification.

The full Si- and Mn-homogenization requires a high temperature treatment because of a large segregation dimensional scale. Calculation showed that even after 24 hr of heat treatment at 920°C (1688°F) the structure still was not fully homogenized. Additional calculations showed that the increase in graphite nodule count and the decrease in the average neighboring distances between nodules from 50 µm to 30 µm decreased the required homogenization time from 24 hr to 12 hr. The degree of segregation also depends on an average concentration of alloying element in cast iron. Decreasing Si content in ductile iron substantially decreased Si-segregation originating during solidification, and the maximum of Si concentration level near spherical graphite (Fig. 4). This data was used for the design of experimental parameters for homogenization heat treatment.

LOW TEMPERATURE CHARPY IMPACT ENERGY

Charpy impact test was performed for v-notched specimens cut in the longitudinal direction from a continuously solidified ductile iron bar with 2.5% Si (Table 1). Depending on the radial position, specimens had a graphite nodule count from 50 to 450 nodules per mm² and a neighboring nodule distance from 30 to 60 µm for the same average alloy chemistry (Fig. 5a).
ferritic in the near-surface layer to pearlite/ferrite mixture in the central regions (Fig. 5b).

Microstructures of low-Si ductile iron (Table 1) in 4 in. wall thickness sand castings are shown in Fig. 6 for as cast condition and after ferritizing/homogenizing heat treatment. The relationship between nodule count and neighboring distance for this ductile iron is shown by the red marker in Fig. 5a. Heavy section sand casting has similar graphite nodule count and distribution when compared to the central zone of continuously cast bar, while in the first case, the shape of individual nodules had some distortions (Fig. 6a).

Charpy impact tests of continuously cast ductile iron specimens taken from different bar locations were performed at room temperature and at -20°C (-4F). The specimens were tested in as cast conditions as well as after two types of heat treatment: (i) only ferritization for 2 hr at 850°C (1562°F) and (ii) homogenization during 24 hr at 920°C (1688°F). The last test regime was chosen based on predicted Si-homogenization parameters. After these two heat treatments, ductile iron was slowly cooled in a furnace to 600°C (1112°F) followed by chilling in air.

![Graph showing nodule graphite parameters in continuously cast bar.](image)

Fig. 5. (a) Graph shows nodule graphite parameters in continuously cast bar (red marker showed data for 4 in. wall thickness sand mold casting). Structures and fractures at 10 mm, 30 mm, 50 mm, and 80 mm from cast surface to center of continuous cast bar are pictured from left to right: (b) etched as cast microstructure and (c) impact fracture of specimens tested at room temperature.
For the as cast condition, room temperature impact energy decreased proportionally with decreasing graphite nodules count (Fig. 7a). At -20°C (-4F) test, specimens with less than 450/mm² nodule count had a brittle fracture and showed very low impact energy. Three factors simultaneously affected these results: (i) graphite nodule count, (ii) the differences in metal matrix structure and (iii) Si-segregation. An excessive negative Si-segregation in the ferrite “halo” around nodules in ductile iron with low nodule count promoted ferrite brittleness. Ferrite in the same ductile iron with larger nodule count and having lesser Si-segregation had a typical ductile fracture (Fig. 5c).

A comparison of -20°C (-4F) Charpy impact energy of the specimens from continuously cast bar after different heat treatments is given in Fig. 7b. In this case, all specimens had approximately the same ferritic matrix and only two factors, including graphite nodule number/distance and Si-segregation, could have affected these test results. The short ferritzing heat treatment, which has a minor effect on Si-segregation, increased the values of impact energy for all nodule counts when compared to the as cast condition. At the same time, the ferritzing treatment did not eliminate the decrease in impact energy observed in ductile iron with low nodule counts.

Finally, the test results after full homogenization were affected only by graphite nodule counts. It is important to note that in this case the nodule count had the opposite effect on impact energy (Fig. 7b). Decreasing nodule count and the associated increase in nodule neighboring distances increased the impact energy of fully homogenized ductile iron. These tendencies were observed in fully homogenized ductile irons with variations in graphite nodule count from 100/mm² to 450/mm².

An additional test of fully homogenized ductile iron with 2.5% Si was performed to determine the effect on nodule count on the ductile to brittle transition temperature (DBTT). In this case, specimens were taken from near the surface and at 1/3 radius positions of a continuously cast 10 in. diameter bar and had on average 435/mm² and 123/mm² nodule counts. As in previous tests, low nodule count ductile iron had higher Charpy impact energy from room temperature to -20°C (-4F) (Fig. 7c). At the same time, the high silicon level limited DBTT between -20°C (-4F) and -40°C (-40F) for both structures. Specimens with finer spherical graphite showed a slightly higher impact energy value at -60°C (-76F) while fractures were brittle in both cases at low temperature.

The results of testing the low silicon (1.5% Si) ductile iron in heavy 4 in. sections in the as cast condition and after two different heat treatments (ferritzing and homogenizing) are presented in Fig. 8. The metal matrix had a ferrite/pearlite mixture (Fig. 6c) because ductile iron had low silicon. The ferrite/pearlite structure resulted in low impact energy. Ferrizting heat treatment of low-Si ductile iron twice increased impact energy while fully homogenized specimens showed superior impact energy and DBTT below -40°C (-40F). In this case, 10 hr of heat treatment at 920°C (1688F) was chosen based on diffusion calculations. It is interesting to note that these properties were obtained for ductile iron in heavy section sand casting with the spherical graphite shape that was not ideal (Fig. 6a).

DISCUSSION

The effect of silicon on the deformation properties of BCC Fe was studied by using ab-initio calculations of cleavage and slip energies for the Fe15Si supercell. In this system, the Si atom was substituted for one of four Fe atoms at (001) plane. The calculated cleavage energy for pure BCC Fe is 4.952 J/m² that corresponds to the (001) surface energy of 2.476 J/m². The calculated value is in good agreement with previous theoretical data (2.435 J/m² and 2.47 J/m²) and experimental results (2.41 J/m²). Silicon atoms on the (001) plane decrease the cleavage energy down to 4.684 J/m².

A slip simulation was performed for the <100> direction on the (001) plane. The maximum generalized stacking fault energy occurs at 0.5 <100> displacement and it corresponds to unstable stacking fault energy, G_{SF}. The values of G_{SF} calculated for pure BCC Fe and Fe15Si1 are shown in Table 2. G_{SF} slightly increased with Si addition.
Fig. 7. These graphs show the Charpy impact energy of continuously cast ductile iron with 2.5% Si: a) effect of graphite nodule count room temperature and -20°C test of as cast specimens, b) comparison of as cast, ferritized and homogenized specimens tested at -20°C and c) ductile to brittle transition in homogenized ductile irons with two nodule counts.

Fig. 8. The graph shows the effect of different heat treatments of heavy section (4 in.) sand cast low silicon ductile iron (1.5% Si) on v-notch impact energy at different temperatures.

Table 2. Comparison of Cleavage ($G_C$) And Unstable Stacking Fault ($G_{SF}$) Energies

<table>
<thead>
<tr>
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<th>$G_C$, J/m²</th>
<th>$G_{SF}$, J/m²</th>
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<tbody>
<tr>
<td>Fe-BCC</td>
<td>4.952</td>
<td>1.54</td>
</tr>
<tr>
<td>Fe15Si1</td>
<td>4.684</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Therefore, our calculations predict that silicon decreases the cleavage energy, $G_C$, and increases the unstable stacking fault energy, $G_{SF}$. These two changes favor an increase in the brittleness, because within the Rice-Thompson model the tendency to brittle or ductile behavior is controlled by the $G_C/G_{SF}$ ratio. It should be noted that the change in cleavage energy is the largest contribution in reducing $G_C/G_{SF}$ ratio. Similar results were predicted based on the calculations of elastic moduli for Fe-Si alloy, where bulk modulus $B$ reduces by about 5%, while shear modulus $G$ increases by 2.8% with Si doping. The $B/G$ ratio also reflects the trend towards brittleness. It can be concluded that the decrease of cleavage characteristics under Si doping is mainly responsible for the brittle behavior of Fe-Si alloy.

The role of high average Si concentration and negative Si segregation is critically important for low ductility and high DBTT in heavy section castings. At very slow cooling rates, when the structure has a low nodule number per unit area and large graphite neighboring distance, high Si concentrations on the graphite/austenite boundary are the combined result of these factors. Decreasing the Si-alloying level along with the homogenization heat treatment provide for superior low temperature mechanical properties in ductile iron for heavy sections.
Figure 9 compares two ductile irons with approximately the same graphite nodule population density, but different silicon contents. In spite of not having the ideal graphite nodule shape in the low Si sand cast ductile iron when compared to high Si continuously cast ductile iron, the first one has an advantage for low temperature applications after full homogenization.

![Graph showing Charpy impact strength vs. temperature for different silicon contents](image)

**Fig.9. The graph shows the comparison of V-notch impact strength of homogenized ductile irons with 1.5% Si (920°C, 10 hr) and 2.6% Si (920°C, 24 hr).**

**CONCLUSIONS**

It was shown that specific microstructural features originate during solidification such as graphite morphology and Si segregation. Both of these features affect the impact toughness and ductile-to-brittle transition temperature (DBTT). In as-cast condition, regular composition ductile iron (2.5% Si) with finer graphite structure exhibited higher toughness when compared to ductile iron with large graphite nodules. On the contrary, in Si-homogenized ductile iron, the significant increase in impact toughness and a decrease in DBTT were observed in specimens with large graphite nodules and neighboring nodule distances.

Lowering the Si content in conjunction with a Si homogenization heat treatment improved the low temperature impact toughness of heavy section ductile iron castings. The experimental results showed the possibility of significantly reducing the DBTT temperature and increasing impact toughness. The suggested processing optimization provided superior low temperature properties in ductile iron.

Thermodynamic analysis and diffusion modeling solidification segregation together with first principle calculations of shear and cleavage of the BCC Fe lattice, alloyed with Si, were used to understand the brittleness phenomena and can be applied in the future for alloy design.

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