THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Microstructure Formation During Solidification and Solid State Transformation in Compacted Graphite Iron

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Compacted graphite iron (CGI) is rapidly becoming an attractive alternative material for engine components in the automotive industry, replacing lamellar graphite iron (LGI) in applications where high mechanical strength is desired. However, the gain in mechanical strength comes with a cost; thermal conductivity, process control and machining are three areas that are more challenging for CGI. This generates a need for research regarding various aspects concerning CGI. In this thesis the microstructure formation during solidification and solid state transformation will be the focus of interest.

The phase transformations relevant for microstructure formation of importance to properties in CGI were studied. Experiments were performed in an industrial foundry giving this research direct relevance to regular production of CGI castings.

Solidification of the grey (graphite/austenite) eutectic will be discussed, focusing on some relevant aspects influencing the graphite morphology of CGI. The formation of graphite nodules has been investigated by studying colour-etched microstructures. In a material containing mainly CGI cells it was found that nodules form either early during solidification as a consequence of high undercooling or late in the solidification sequence due to a combination of high undercooling and segregation of nodularising elements. Solidification of the white (cementite/austenite) eutectic was studied using chill wedges and the influence of some alloying elements on the amount of carbides was examined. To further enhance the understanding of carbide formation in CGI a commercial casting simulation software was used to correlate real castings to simulations. It was found that the alloying elements investigated influence the carbide formation in a similar way as in other graphitic cast irons and that high nodularity CGI is more prone to chill formation than low nodularity CGI. The solid state transformation was studied and a deterministic model was developed. The model divides a eutectic cell into layers, in order to take into account segregation of alloying elements, which was observed to be influential for the ferrite growth. Moreover, the effect of alloying elements on mechanical properties (tensile properties and hardness) was evaluated. Properties were correlated to microstructural features originating from both solidification and solid state transformations. The trends found generally confirmed previous results regarding properties in graphitic cast irons.

Keywords: Cast iron, CGI, Microstructure formation, Mechanical properties, Modelling, Solidification, Solid state transformation
MICROSTRUCTURE FORMATION DURING SOLIDIFICATION AND
SOLID STATE TRANSFORMATION IN COMPACTED GRAPHITE IRON

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Mathias König
Jönköping, April 2011
SUPPLEMENTS

The following supplements constitute the basis of this thesis. The supplements denotations and references are followed by a description of the distribution of work.


König was the main author, Svensson, Wessén and Diószegi contributed with advice concerning the work. Diószegi performed the thermal analysis and helped with evaluation of the thermal analysis results


König was the main author, Svensson and Wessén contributed with advice concerning the work


König was the main author, Svensson developed the models, provided the simulation code and contributed with advice concerning the work


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INTRODUCTION

CHAPTER 1

CHAPTER INTRODUCTION

What is cast iron? What distinguishes compacted graphite iron from other cast irons? What are the industrial applications of the material? This chapter aims to provide a background for the reader regarding the topic at hand. Furthermore, issues that will be covered in the summary of results and discussion will be introduced and related to previous research.

1.1 BACKGROUND

Since the industrial revolution during the 18th and 19th centuries development of technology has been the main enabler for society's progress. Today the engineering industry consists of an incalculable amount of companies that are integrated with society to such an extent that they form the platform for the welfare of society in most developed countries. The common denominator for these companies is that they all rely on technology originating from many years of research and development.

One of the most research and development intense industries is the automotive industry. Historically development has been concerned with increasing performance and comfort for the driver. Nowadays the driving force for development is more and more shifting towards environmental considerations, where better fuel economy and lowered exhaust emissions are being considered amongst the main competitive advantages of a vehicle. For the heavy truck industry the European emissions standard defines acceptable emissions of greenhouse gases and particulate matter. A progressive increase in the restrictions of emissions has been ongoing, starting with the Euro 1 bill in 1992 up to Euro 6 that is scheduled to enter into force from 31st of December 2013 [1]. To accommodate the above restrictions the design of the diesel truck engine must be improved. From a material development point of view this means lighter material and/or higher mechanical properties in the engines to cope with increasing combustion pressures. One plausible route involves changing from lamellar graphite iron (LGI) to Compacted graphite iron (CGI), which offers significant increase in mechanical properties [2].

It should however be stressed that the transition from LGI to CGI is accompanied by numerous challenges which concern; foundry personnel, because of the complex process control associated with CGI; engine designers, who must redesign the engine to accommodate the changes in both mechanical and physical properties. Finally, also manufacturing engineers, must rethink their approach to the machining operations associated with the new engine material.
1.2 CAST IRON

This thesis will mainly deal with CGI, however to obtain an overview the most common cast iron grades will be introduced. A further purpose of the overview is to present the differences between the graphitic cast irons. This will be a reoccurring theme in the thesis, when explaining microstructure formation in CGI.

Cast iron is an alloy consisting of iron, carbon and, with few exceptions, silicon. The metal is very versatile and it is possible to obtain a wide range of both mechanical and physical properties by adjusting alloying content or by heat treatment. To develop an understanding of cast iron the binary Fe-C equilibrium phase diagram is commonly studied, Figure 1 [3]. For the binary case cast iron is defined as having a carbon content exceeding 2 wt%. From a microstructure point of view this means that a carbon-rich phase will precipitate during solidification. For grey, or graphitic, cast irons this carbon-rich phase will be graphite and for white, or carbidic, cast irons the carbon-rich phase will be cementite (Fe₃C), also known as iron carbide. The other microstructure constituent formed during solidification will be austenite. At about 4.3 wt% C the melt solidifies as an irregular eutectic containing austenite and graphite or cementite. To take into account the influence of certain alloying elements on the required carbon content to reach the eutectic composition the carbon equivalent (CE) value is commonly used. The CE can be calculated as [4]:

\[
CE = \%C + \%Si/3 + \%P/3
\]

Figure 1: A binary Fe-C phase diagram. The phase diagram was obtained using Thermocalc with the TCFE1 database [3].
If the CE is below 4.3% the composition is said to be hypo-eutectic, which means that primary austenite will form prior to the eutectic reaction. If the CE is higher than 4.3% the composition is said to be hyper-eutectic, and a primary phase of graphite/cementite will precipitate prior to the eutectic reaction.

Consequently the structure after solidification is composed of a primary phase (depending on composition) and a eutectic. However the matrix material will be severely changed during the solid state transformation. The solid state transformation, which starts with the formation of ferrite at approximately 738°C for the binary case, will give the material its room temperature microstructure [5]. Depending mainly on composition, cooling rate, and the solidification structure, austenite in the structure will transform to either ferrite and graphite or pearlite.

1.2.1 Classification of cast irons

As cast iron is a historically significant material, the number of cast iron grades is high. In recent years, since the arrival of spheroidal graphite iron (SGI) in the late nineteen-forties [6], the introduction of new cast iron classes used in industrial applications has accelerated. The classic way used to distinguish between different cast irons was based on the appearance of the fracture surface. Two different classes were found:

- **Grey**: The graphite/austenite eutectic gives this grade its characteristic appearance.
- **White**: In this case the cementite/austenite eutectic causes the fracture surface to become white.

Today the classification of cast irons is aided by the development of the microscope, which allows us to study the microstructure of the material and thus differentiate between classes based on their microstructure. Of particular interest to the automotive industry are the grey cast irons mentioned above, and these are commonly classified according to the shape, or morphology, of the graphite in the structure. Three classes are most common:

- **Lamellar graphite iron (LGI)**: The graphite is present as lamellas, or flakes, Figure 2a. LGI is commonly termed grey iron as this was the original graphitic cast iron.
- **Compacted graphite iron (CGI)**: The graphite particles have a compact or wormlike shape (this grade is also known as vermicular graphite iron), Figure 2b.
- **Spheroidal graphite iron (SGI)**: The graphite is present as spheroids, or nodules, Figure 2c. SGI is sometimes referred to as ductile iron, or nodular cast iron.

Figure 2: Difference in graphite morphology. a. Lamellar graphite [7], b. Compacted graphite, c. Spheroidal graphite.

These are the main graphitic cast iron classes and the cast irons which will be discussed in this thesis. However other classes also exist, which are distinguished by differences in
microstructure formed during casting or as a consequence of heat treatment. Some of the most industrially important classes include:

- **Austempered ductile iron (ADI):** By employing a so called autempering heat treatment the matrix of a SGI can be altered and ADI can be obtained. The austempering heat treatment results in an ausferritic matrix.
- **Mottled iron:** The carbon rich phase in the material is a mixture of graphite and cementite, the structure is formed during casting.
- **Malleable iron:** This is an initially white cast iron that has been heat treated to also contain a certain amount of graphite.

To distinguish between the graphitic (grey) cast irons a classification based on the acceptable graphite morphology will be presented. This has been defined in various standards, e.g. by VDG, ASTM and ISO\(^*\) [8-10]. The standard used here will be the one set forth by the International standard organization, designated ISO16112:2006 [10]. This standard stipulates that at least 80% of the graphite particles viewed on a two dimensional polished surface should have a compacted shape, and less than 20% should have a more round shape, to be classified as CGI. No lamellar shaped graphite particles are permitted. To simplify the determination of which particles have a compacted shape, the standard uses a roundness shape factor (RSF) defined as:

\[
RSF = \frac{A}{A_m} = \frac{4A}{\pi l_m^2}
\]

Where \(A\) is the area of the graphite particle seen on a polished surface, \(l_m\) is the maximum length of the graphite particle and \(A_m\) is the area of the circle with the diameter \(l_m\). The RSF is subsequently used to divide the graphite particles into three different groups. RSF values between 0.625 and 1 are defined as nodules, between 0.525 and 0.625 are defined as intermediate and values below 0.525 are defined as compacted. Particles having \(l_m\) smaller than 10 \(\mu m\) are excluded from the calculations. The nodularity is calculated using these values, as follows:

\[
\%\text{Nodularity} = \frac{\sum A_{\text{nodule}} + 0.5 \sum A_{\text{intermediate}}}{\sum A_{\text{all-particles}}} \times 100
\]

Where \(A_{\text{nodule}}\) is the area of the graphite particles classified as nodules, \(A_{\text{intermediate}}\) is the area of the particles classified as intermediate shaped and \(A_{\text{all-particles}}\) is the area of all particles exceeding 10 \(\mu m\). Thus the nodularity will range from 0 % for an ideal CGI to 100 % for an ideal SGI.

\(^*\) VDG: Verein Deutscher Gießereifachleute
ASTM: American Society for Testing and Materials
ISO: International Organization for Standardization
1.3 MICROSTRUCTURE FORMATION IN CGI

The microstructure in cast irons mainly forms during the two major phase transformations which the material passes through while cooling down from the liquid phase to room temperature, hence solidification and solid state transformation as illustrated in Figure 3.

1.3.1 Solidification

As seen in Figure 3 the solidification starts with precipitation of a primary phase, for the case seen in the figure the primary phase was austenite, implying that the composition for the solidifying melt is hypo-eutectic. In most CGI applications a slightly hypo-eutectic composition is preferred. The primary austenite grows as rather thin dendrites with a high growth rate until they impinge. Following conventional solidification theories the austenite commonly nucleates at the mould wall resulting in columnar growth and at a slightly lower temperature the austenite can nucleate on heterogeneities in the melt leading to equiaxed growth. The thin dendrites grow rapidly and form a network of dendrites. Each dendrite forms a rather large austenite grain, which can be studied using a recently developed metallurgical technique (direct austempering after solidification or DAAS) [11]. After impingement of the dendrites growth will continue by dendrite arm coarsening [12]. During growth the dendrites will reject carbon to the melt, and when the melt reaches the eutectic composition the eutectic is able to nucleate.

![Solidification](image.png)

Figure 3: Cooling curve showing the two main phase transformations occurring in cast iron.

The composition in the austenite at the austenite/melt interface will follow the solidus line in the phase diagram (Figure 1) resulting in the above mentioned rejection of carbon. If carbon diffusion in the solid is not rapid enough this will result in a concentration gradient in the solidified material, which is commonly called segregation. For the case of carbon this will mean that the last to freeze areas of the melt, i.e. where the eutectic is situated will be enriched in carbon. The main alloying elements normally found in cast irons segregate; and some are enriched in the first to solidify areas, whereas others segregate to the last to freeze areas. To describe the segregation a partition coefficient is usually defined. The partition coefficient, K, is defined as [12]:

Where $C_s$ is the concentration in the solid and $C_l$ is the concentration in the liquid of the alloying element in question. Among the most important alloying elements Mn, Cr, Mo and Mg segregate to the last to freeze areas (i.e. $K<1$), similarly to C, while Si and Cu will preferably be incorporated by the solid phase ($K>1$) [13]. Segregation is important to many phenomena discussed in this work, and it is possible to study the segregation pattern in solidified cast iron using colour etching techniques [14]. An example of this can be seen in Figure 4a where it is possible to distinguish austenite dendrites from the surrounding structure. The colour etching reveals the segregation pattern of Si, and the light blue colour associated with the dendrites means that these areas are rich in Si and have solidified early. Studying the figure further it is possible to see that the light blue colour gradually changes to darker blue, then turns dark brown and finally in the last to freeze areas the structure is light brown. The above mentioned etching technique will be discussed in further detail in Chapter 2.3.3.

As the temperature drops below the eutectic equilibrium phase transformation temperature the eutectic is able to form according to the phase diagram. However, a departure from equilibrium is necessary to initiate solidification, hence some undercooling is required [15]. For the eutectic reaction to start both austenite and graphite must nucleate. Nucleation of graphite has been studied in some detail for LGI and SGI [16, 17], however, for the case of CGI this issue has not been extensively studied. A study by Tartera et al. [18] noted that graphite nuclei in CGI contained MgS and CaS similar to nuclei found in SGI. When both graphite and austenite have nucleated, Rivera et al. [19] reports that growth of the eutectic starts when the graphite nuclei come into contact with austenite dendrites, that grow inside the melt regardless of whether the composition is hypo-, hyper- or purely eutectic.

During growth of the eutectic there are large differences between LGI, CGI and SGI, resulting in the different graphite morphology seen in Figure 2. The eutectic grows due to a diffusion process that transports carbon to the graphite phase and iron to the austenite phase. In LGI the graphite and austenite grow cooperatively, meaning that graphite and austenite grow in contact with the melt side by side and radially outwards to form a spherical eutectic.
cell. This growth is rather rapid as the diffusion process, which controls the growth rate, takes place in the liquid in front of the solidification front. For the case of SGI the graphite nodule is encapsulated by austenite at an early stage, leading to a situation where the carbon diffuses through the austenite layer surrounding the graphite (divorced eutectic). The growth rate in this case is significantly lower as the carbon has to diffuse through a solid and the diffusion distance is larger than in LGI [15]. Similar to LGI, CGI grows in spherical eutectic cells (Figure 4), however in this case the cooperation between austenite and graphite is not as strong as in LGI. This means that graphite in CGI is more likely to lose contact with the melt during solidification. Using interrupted solidification experiments, thin liquid channels through the austenite layer surrounding the graphite can be seen [20, 21]. The liquid channels imply that graphite has grown in contact with the melt, but the austenite has grown past the graphite and almost encapsulated the graphite particle.

![Graphite Lattice](image)

Figure 5: The hexagonally close packed lattice of graphite [22].

The appearance of the graphite shape is the most obvious difference between LGI, CGI and SGI. When examining the graphite for the different cast iron grades it can be seen that LGI mainly grows along the A-axis of the graphite lattice, while SGI mainly grows along the C-axis, Figure 5. In the same study it was found that the growth direction continuously changed between the C- and the A-axis in CGI [23]. It is well known that Mg affects the graphite morphology and therefore by adding relatively small amounts of Mg it is possible to cause a CGI melt to solidify as SGI, thus Mg has a nodularising effect on the melt. It has, however, been shown that it is not the Mg that has a direct effect on the melt, but rather the elements that Mg neutralize when added. It is mainly oxygen and sulphur that are mentioned as elements that lower the nodularity, and by adding Mg these elements are neutralized [22, 24]. Further evidence for this was provided when an ultra-pure cast iron melt, free from O and S and Mg, was seen to obtain a SGI structure when solidified [25].

There is however no clear consensus about why O and S lower the nodularity. It has been suggested that O and S are preferably absorbed on the prism face of the graphite lattice, facilitating a high growth rate along the A-axis. The normally faceted prism face of the graphite changes to a non-faceted face and as a consequence the growth rate increases...
significantly. This means that the main growth direction will be along the A-axis and this corresponds to the case found in LGI [22]. Another mechanism that would explain the changes in graphite morphology caused by O and S is based on the influence these elements have on surface energy. Measurements have shown that SGI melts have higher surface energy than LGI melts, with CGI intermediate between these two types [26, 27]. It is suggested that the surface active elements are absorbed on the edge planes between graphite and the melt, which alters the interfacial energy and contact angle. If sufficient amounts of O and S are present, the surface energy will decrease and the growth rate of the graphite phase will increase resulting in graphite lamellas growing into the melt and a lowered nodularity is obtained [27]. Several other theories regarding the influence of O, S and Mg on graphite morphology exist [28, 29].

The graphite morphology is also dependant on the cooling conditions during solidification, resulting in an increased nodularity where high solidification rates can be expected [30, 31]. This has been attributed to defect controlled graphite growth mechanisms being dominant compared to impurity controlled growth mechanisms (due to O and S) at high undercooling, i.e. high solidification rates [22]. Similarly to adjusting the Mg content it is possible to obtain the whole range of graphite morphology, from lamellar to spheroidal, by altering the cooling rate [31].

If high solidification rates, resulting in excessive undercooling are attained during solidification the temperature will drop below the metastable eutectic temperature, enabling formation of the white (cementite/austenite) eutectic. CGI is reported to be susceptible to carbide formation, due to the solidification characteristics of the grey (graphite/austenite) eutectic [32]. Certain solidification conditions should be satisfied in order to obtain a good compacted graphite morphology. The nucleation conditions in the melt should be unfavourable, resulting in a low number of eutectic grains, and the growth should also be unfavourable [31]. Consequently the eutectic undercooling will be substantial and rate of recalescence will be high. As noted above, high undercooling during solidification increases the possibility of the temperature dropping below the metastable eutectic temperature, enabling nucleation of the white eutectic.

Depending on the cooling conditions, several typical carbide formation cases are possible:
If a rather slow cooling is obtained in combination with limited numbers of growing grains (equivalent to low inoculation) there is a risk of obtaining segregation carbide formation. Figure 6a. In the figure it can be seen that segregation affects both the stable and metastable eutectic transformation temperatures, resulting in carbide formation towards the last parts of the solidification sequence. This means that when the microstructure is studied these carbides can be found between graphite/austenite eutectic cells, in last to freeze areas.

If high cooling rates are obtained, which typical of the case in thin sections of a component, the temperature will drop below the metastable eutectic transformation temperature at an early stage and the main part of the melt will solidify as white eutectic Figure 6b. Note that in this situation the temperature is also well below the stable eutectic transformation temperature, so that there will be a substantial driving force for growth of the grey eutectic. However as growth rate for the white eutectic is several orders of magnitude higher than for the grey eutectic, the main part of the structure will become white [33].

In Figure 6c a mixture of the prior two scenarios is found. The cooling conditions are somewhat less extreme in this case than in the previous case, resulting in formation of white eutectic and grey eutectic, but due to recrystallization the temperature will increase above the metastable eutectic transformation temperature and the white eutectic will not be able to grow. This will continue until the end part of solidification where segregation may cause segregation carbides to form.

The influence of alloying elements on the stable and metastable eutectic transformation temperatures are important to the tendency of the melt to solidify either with the cementite/austenite or the graphite/austenite eutectic. The influence of the alloying elements is commonly divided into two classes: graphitizers and carbide promoting elements. Among the most significant graphitizers are Si, Cu, and Al while Cr, V and Mn are potent carbide promoting elements [5]

1.3.2 Solid state transformation

During the solid state transformation cast irons obtain their room temperature structure. During the solid state transformation the matrix will change from an austenitic structure to either both ferrite and graphite, according to the equilibrium phase diagram, or to pearlite, according to the metastable phase diagram. The solid state transformation is of great importance to mechanical properties such as the ultimate tensile strength of the material which can vary by more than 100 MPa, depending on whether the matrix is ferritic or pearlitic.

Under equilibrium conditions the solid state transformation takes place at 738°C with the formation of ferrite and graphite for the binary Fe-C alloy, however some alloying elements are always present, which affects the transformation temperature. In a multi element case a tri-phase interval is seen in the phase diagram, Figure 7 [5]. This means that the first ferrite that forms will be found in this area and depending on the temperature varying amounts of ferrite, austenite and graphite will be formed. In the tri-phase interval the ferrite growth process is rather slow and the main part of the ferrite, will form when the temperature decreases below the lower critical transformation temperature, \( T^\alpha \). Below the lower critical temperature there is a driving force for carbon to diffuse to the graphite, which will give rise to a ferrite layer forming around the graphite. In SGI this will manifest itself as the characteristic bull's eye structure, and for the case of CGI a typical structure can be seen in Figure 4b, where it is seen that the graphite is surrounded by ferrite.
During ferrite growth below the lower critical temperature the graphite acts as a carbon sink in the microstructure. After ferrite has been nucleated on the graphite, the carbon will diffuse through the ferrite layer and be absorbed by the graphite. The driving force for carbon diffusion will increase as the difference between $C_{\text{a}gr}^{\alpha}$ and $C_{\text{c}\gamma}^{\alpha}$ (Figure 7) increases, i.e. the driving force increases as the undercooling increases [34]. Furthermore, as seen in Figure 7 at increasing undercooling there will be an increase in the driving force for carbon to diffuse from the ferrite/austenite interface into the austenite, which will also contribute to the growth of ferrite.

As indicated above, graphite will play an important part in influencing the ferrite growth and there are substantial differences in ferrite formation between LGI, CGI, and SGI [35, 36]. This was related to the rate at which carbon can be absorbed by graphite, which in turn depends on the number of exposed edges along the A-axis (prism planes). The significance of the exposed A-axis edges is that it is energetically significantly more favourable to add carbon atoms to these planes than to the edges of the C-axis, implying that having a large amount of exposed A-axis edges will lead to favourable conditions for ferrite formation [25]. In SGI the graphite nodules have grown in a circumferential manner with a large number of edges of the A-axis exposed and significant amount of growth defects, so that the carbon atoms can easily be absorbed during ferrite growth. For conventional LGI the opposite is the case, the graphite has grown without significant amounts of defects, and the edges of the A-axis are only exposed on the edges of the graphite particle, Figure 8 [36]. In CGI the growth direction frequently changes from the A-axis to the C-axis and large numbers of growth defects can be seen in the graphite. This will lead to a situation where ferrite growth in CGI is more comparable to SGI than LGI.

The size and dispersion of the graphite particles will significantly influence the ferrite growth. Assuming that the alloying content is constant the graphite fraction in the material will be approximately the same. However, the graphite particles can be either small and numerous or coarse and few, depending on solidification conditions. Furthermore, the graphite particles
are typically not homogeneously distributed in the matrix. As noted above ferrite growth is dependent on carbon diffusion through the ferrite layer, implying that the nature of the ferrite layer is significant for the process. If the ferrite layer is thin the diffusion distance for the carbon is relatively short and the process is quicker, than if the ferrite layer is thick. A finer graphite structure will lead to a higher graphite surface area/volume ratio than a coarse structure. This means that a material with a finer graphite structure will have a larger graphite area where the ferrite is able grow and to obtain a certain total ferrite amount in the matrix the ferrite layer does not have to be as thick as in a material with a coarse graphite structure.

The nodularity can also be related to this discussion as spheroids (nodules) found in SGI have a low graphite area/volume ratio, implying that SGI is less prone to ferrite formation than CGI in this aspect [37].

The ferrite growth is subsequently interrupted by pearlite formation when the temperature drops below the metastable eutectoid transformation temperature, which occurs at 727°C for the binary alloy [5]. Pearlite growth is not dependant on the graphite morphology and growth is usually described by procedures developed for steels, see for instance work by Al-Salman et al. [38] on Fe-C-2%Si steel.

Some of the common alloying elements in cast irons have considerable influence on the solid state transformation. The effect is analogous to the effect seen on solidification, i.e. the elements that have a graphitising effect during solidification commonly promote phase transformation according to the equilibrium phase diagram also in the solid state. For instance Si and Al promote ferrite formation, while Mn and Cr promote pearlite [5]. Some notable exceptions to this exist however, and Cu and Sn are known as graphitisers during solidification but in the solid state they promote formation of pearlite. It is reported that Cu and Sn preferably absorb on the graphite/austenite interface where they act as diffusion barriers to carbon that needs to diffuse to the graphite in order for ferrite to form [39-41].

As the austenite is completely transformed and the solid state transformation is completed the material has obtained its room temperature microstructure. This also brings this short summary of microstructure formation to a close and the following chapters will continue to explore the work done within the limits of this thesis.
CHAPTER 2

RESEARCH APPROACH

CHAPTER INTRODUCTION
This chapter aims to answer two questions, that explains the essence of this work. In the words of Prof. Doru Stefanescu these questions are “Why?” and “Who cares?” The “Why?” question refers to details of the work, why has the research been carried out in the way it has been and what are the specific research questions. The “Who cares?” question adopts a more global perspective and aims to explain who might be interested in the work, and whether the research is useful.

2.1 AIM AND PURPOSE OF THE WORK
The general purpose of this work has been to investigate microstructure formation in CGI, and what implications this has for mechanical properties. This is important especially in the heavy truck industry where CGI is being considered as the next generation engine material. Development in the automotive industry in general, but also for truck manufacturers in particular is driven by environmental legislation. To decrease the environmental impact of modern trucks it is imperative to limit the amount of gaseous and particulate pollutants in the exhaust of the vehicle. The main way to achieve this is to increase the combustion pressure in the engine, which requires higher mechanical properties than the current engine design using LGI permits. This implies that a change in engine material is approaching, with CGI being the main candidate. However the shift in engine material is not straightforward, CGI exhibits different physical and mechanical properties, so that great effort is required to modify the engine design, the casting process and machining of the engine components. As a consequence these areas are the focus of ongoing research, or recently finished projects [42, 43].

The focus of this thesis however is to study the microstructure formation in CGI, which in turn determines a majority of the properties of the material. Compared to other cast irons CGI is characterized by its section sensitivity, leading to a wide variety of properties in a cast component. Among the features that are important is the solidification of the graphite eutectic, which determines the graphite morphology of the material. Several parameters are important and the solidification rate (which is related to section thickness) has a major influence on the nodularity and thus properties. Furthermore the carbide eutectic, which also is closely related to section thickness will be studied in order to determine the chill tendency as well as to understand the formation of inverse chill and segregation carbides. To obtain a complete view of the microstructure formation it is necessary to study the solid state
transformation. This phase transformation is of great importance to the room temperature properties as the matrix obtains its final structure at this stage.

A general aim of this thesis is to increase our knowledge base and understanding regarding the wide variations in microstructure and properties found in a CGI component. To further aid in making the knowledge generated accessible, models describing microstructure formation during the phase transformations have been developed. The aim and purpose of the work will be further concretized with three research questions

### 2.2 RESEARCH QUESTIONS

Three research questions have been guiding this work and have governed the research methods used to achieve the aims set forth earlier in the chapter. The questions were divided into three generic levels, resulting in a progression in the understanding and increasing depth of scientific relevance. The generic levels dedicated to the microstructure formation during solidification and solid state transformation in CGI were: characterize, understand, and model.

- CGI is often considered as a transitional structure between LGI and SGI, implying that to understand microstructure formation in CGI it is relevant to study the differences between LGI, CGI and SGI. Therefore the basis of the characterization will be the question: **What distinguishes microstructure formation in CGI from other graphitic cast irons?** (all supplements)

- Substantial research has been aimed at understanding how the graphite shape is obtained during solidification. The present work does not focus on the mechanisms responsible for the change in graphite morphology, on an atomic scale, but rather tries to explain some central factors responsible for these changes. Specifically graphite nodules in the structure are of interest, as they are responsible for dramatic change in properties, both mechanical and physical. **Why do nodules form, when during the solidification sequence are the nodules likely to form, and where in the structure are the nodules likely to form?** (supplement I) A notable difference between LGI, CGI and SGI is the tendency for chill formation, therefore a relevant question would be: **What is responsible for the differences in chill tendency when comparing CGI to LGI and SGI?** (supplements II and III) Another difference is seen when ferrite growth is compared, prompting the question: **How does the graphite morphology affect the solid state transformation in CGI?** (supplement IV)

- To fully take advantage of the knowledge gained, models and simulations are invaluable tools to spread information to the foundry industry. Mainly two of the above discussed issues will be dealt with from a modelling/simulation perspective. The carbide formation in cast irons is certainly very influential to both properties and from a machining point of view, and hence models describing this are of great industrial usefulness. **How can the carbide formation in CGI be modelled/simulated?** (supplement III) The solid state transformation and ferrite growth in CGI have many similarities to ferrite growth in SGI, however there are also substantial differences. **How can ferrite growth in CGI be modelled/simulated?** (supplement IV)
2.3 MATERIAL AND EXPERIMENTAL PROCEDURE

2.3.1 Material

The experiments described in the following sections were performed in an industrial foundry during the first six months of year 2007. Five alloying parameters were investigated; nodularity treatment level (varied by changing the Mg-content), Cu-content, Si-content, Sn-content and carbide promoter content, the latter varied by altering the levels of Mn, Mo and Cr.

Nineteen heats were cast to study the influence of varying alloy composition, according to Table 1. The melts were prepared in a medium frequency induction furnace from 1100 kg CGI returns, 1400 kg nodular cast iron returns, 300 kg steel plates and 200 kg tin plated steel sheets. The desired alloying content was set before the melt was given its CGI treatment. Subsequently the melt received a base treatment in a 500 kg ladle before Mg-wire and inoculant wire was added using Sintercast process control [44].

Table 1: The chemical composition of the 19 heats. (wt%)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Sn</th>
<th>Cr</th>
<th>P</th>
<th>Mo</th>
<th>S</th>
<th>Mg</th>
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<td>0.007</td>
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<td>4.34</td>
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<td>0.03</td>
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<td>0.04</td>
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<td>0.008</td>
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<tr>
<td>Cem2</td>
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<td>0.60</td>
<td>0.051</td>
<td>0.10</td>
<td>0.015</td>
<td>0.01</td>
<td>0.008</td>
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<td>4.38</td>
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<tr>
<td>Cem3</td>
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<td>0.10</td>
<td>0.009</td>
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</table>

*Carbon equivalent calculated as CE = %C + %Si/3 + %P/3.

The melt was subsequently poured in three different moulds; a sampling cup, a mould containing conical cylinders of three different diameters used for tensile testing and a chill wedge.
2.3.2 Cast sample geometries

The sampling cup was used to perform thermal analysis as well as to evaluate the microstructure of the different heats, Figure 9. The sampling cup was developed and has previously been used in experiments by Elmquist and Diószegi [7]. The cup consists of a sheet metal cup and two protective tubes welded to the cup. The protective tubes are made to fit type-N thermocouples, that can be inserted from underneath the cup. The temperatures were measured in all sampling cups. One thermocouple is placed in the thermal centre of the cup and the other thermocouple is situated close to the cup wall. To obtain different cooling conditions the cup was placed in a mould made of three different materials:

- A furnace refractory, that will be denoted ‘A’. It consists mainly of Al$_2$O$_3$, CaO and Fe$_2$O$_3$. The ‘A’ refractory has a high thermal conductivity which gives the casting a high cooling rate. The high thermal conductivity of the refractory resulted in solidification times of about 255 sec.

- Furan bounded quartz sand, which will be denoted ‘B’, has a thermal conductivity intermediate between ‘A’ and ‘C’ that resulted in a solidification time of about 400 sec.

- A furnace refractory, that will be denoted ‘C’. It consists mainly of SiO$_2$, Al$_2$O$_3$, CaO and Fe$_2$O$_3$. In the experiments a typical solidification time for castings made in this mould material was 1125 sec.

Two of the mould materials; ‘A’ and ‘C’ are furnace refractories produced by Calderys refractory solutions [45].

The tensile test bars were cast in the geometry shown in Figure 10; one casting was made per alloy. The geometry consisted of six conical cylinders of different diameters in order to obtain different cooling conditions. The cylinders were cast in a furan bonded quartz sand mould.
The diameters were Ø20, Ø45 and Ø85 mm at the narrowest section. In Figure 10 the cylinders and the gating system can be seen. There are three cylinders with Ø20 mm resulting in three tensile test bars, one with Ø45 mm resulting in two tensile test bars and one with Ø85 mm resulting in three tensile test bars, which means that 8 test bars were obtained per alloy. The test bars were machined to a gauge diameter of 12.5 mm, with a gauge length of 60 mm. The bars were threaded at the ends.

![Figure 11: The die that was used to cast the chill wedges.](image)

The chill wedge die is made of four 10 mm thick low carbon steel plates, and is shown in Figure 11. To facilitate a two dimensional heat flow from the solidifying wedge two 5 mm thick insulation sheets were placed on two of the faces of the die. The surface of the die that is in contact with the melt during casting (the angled plates) was ground and subsequently coated with a graphite coating. Temperature measurements in the solidifying metal were carried out on one die per chemical composition, i.e. 19 wedges. For each of the 19 wedges cooling curves were recorded along the centre line of the casting at three different heights above the wedge tip (30; 60 and 90 mm). Furthermore the temperature in the die was measured on five occasions, one for each of the alloy parameter series. Three measurements were made in the die, at different locations and at 2, 4 and 6 mm distance from the melt/die interface. The temperature measurements were made using type-N thermocouples. The thermocouples were protected by a protective tube arrangement consisting of a quartz tube supported by a steel tube, surrounding the quartz tube. The arrangement had a total diameter of 2.2 mm.

Due to leakage problems not all wedges were cast correctly. Depending on these problems one or two of the wedges were used to study the fractured surface, while the remaining wedge was used for microstructure analysis.

### 2.3.3 Microstructure analysis

The microstructure of the sampling cups, tensile test bars and chill wedges was evaluated using a Leitz DMRX optical light microscope from Leica and the Qwin image analysis programme. The graphite structure was evaluated on an as-polished surface, using the
procedure described in Chapter 1.2.1 to calculate nodularity. Furthermore the graphite particle density and the area fraction of graphite was measured, for each photomicrograph.

A 2% HNO₃ in ethyl alcohol solution (Nital) was used as etchant to study the matrix structure. In the results the content of ferrite and pearlite in the matrix (excluding the graphite) will be given, implying that adding the percentage of pearlite and the percentage of ferrite in a sample will sum to 100%.

A total of 27 mm² for each of the sampling cups was analyzed with image analysis software.

An etchant containing 10 g picric acid, 10 g NaOH, 40 g KaOH and 50 ml water was used for colour etching to reveal the segregation pattern in the microstructure of sampling cups for the Cu-series. Etching was performed at 110°C for approximately 3 min. The maximum eutectic cell size, fraction eutectic CGI cells and the secondary dendrite arm spacing (SDAS) was measured on the colour etched surface in the sampling cups. To be able to measure data concerning eutectic cells, the cells were coloured as demonstrated in Figure 12 before quantification. After the cells were coloured image analysis was performed using Leica QWin. The SDAS was evaluated as the average of three measurements, and each measurement analysed a minimum of three dendrite arms to evaluate the SDAS. A total of 122 mm² for sampling cups B and C was evaluated, whereas for cup A the structure was not as coarse as for B and C and for this reason it was judged to be enough to evaluate 50 mm² using a higher magnification.

Figure 12: Photomicrograph of colour etched surface, showing eutectic cells. a. original appearance, b. structure illustrating how the cells were coloured to enable image analysis.

Colour etching was also used to evaluate the length of the columnar white zone in the chill wedges. In this case the perpendicular distance from the die wall to the transition from grey to white was measured as in Figure 13a. Measurements were performed on the Cu and Si series on one wedge per alloy and on both sides of the wedge. The length of the columnar white zone was also measured on the fractured wedges. The wedges were cut about 100 mm above the wedge tip and subsequently a notch was made along the height of the wedge to facilitate a fracture in the centre of the wedge. A Canon EOS 1000D camera was used to take photographs of the fracture surfaces where in a similar way to the measurements performed on the colour etched samples the length of the columnar zone was measured, Figure 13b. In the figure a second measure of the chill tendency is illustrated, namely the width of the wedge where the columnar zones intersect. Measurements were made on one or two wedges.
depending on the aforementioned leakage problems and on both sides of the wedge for the case of columnar zone length. A JEOL JSM-7001F scanning electron microscope was used to measure the pearlite lamellar spacing in the sampling cups for the Cem-series. The major part of the sampling cup area was examined. To ensure that the measured lamellas had grown perpendicular to the observed surface the smallest lamellar spacing found was considered to be the correct spacing.

2.3.4 Tensile testing

The tensile tests were performed on a Zwick/Roell Z100 universal testing machine with a 100 kN load cell at room temperature. All tensile tests were performed at a crosshead displacement speed of 0,5 mm/min. The tensile testing at room temperature was performed according to SS-EN 10 002-1. A total of 152 tensile tests were performed and recorded. The extension of the samples was measured using two extensometers: one from Zwick/Roell with 20 mm gauge length and one from MTS with 25 mm gauge length. Due to a defect in the extensometer the elongation was not measured correctly on some of the tensile test samples. As a consequence, some results, related to the elongation will not be included.

![Figure 13: Picture illustrating how; a. The columnar white zone was measured in a colour etched photomicrograph, b. The columnar white zone and the width of the wedge where the columnar zones intersect was measured on a photograph of a fractured wedge.](image)

2.3.5 Hardness testing

Hardness testing was performed on the tensile test bars after tensile testing on the relatively undeformed threaded ends. Brinell-testing was performed a Wolpert Dia Testor 2Rc, due to space restrictions a 2.5 mm ball with 62.5 kg load was used. Three tests per sample were made on each of the tensile test bars. To avoid the influence of deformation hardening the indentations were made approximately 5 mm apart. Brinell hardness measurements were also performed on the sampling cups for the Si and Cu series using a 10 mm ball and a 3000 kg load.
CHAPTER 3

SUMMARY OF RESULTS AND DISCUSSION

CHAPTER INTRODUCTION

This chapter summarises the results and discussion that are included in this work. The chapter will follow a cooling curve from the liquid state to room temperature, discussing the solidification and solid state transformation along the way. Finally, the influence of the microstructure formation on the mechanical properties will be discussed. In the process, the chapter aims to answer the research questions raised in Chapter 2.2.

3.1 ON THE GREY SOLIDIFICATION OF CGI (SUPPLEMENT I)

The work concerning the grey solidification aims to highlight certain aspects that have not been extensively dealt with in research concerning CGI. This means that the focus will be on discussing issues related to these aspects, rather than covering the entire solidification sequence.

3.1.1 Growth rate of the eutectic

One way to understand the kinetics of the solidification is to study the latent heat released using cooling curves. The sampling cup in Figure 9 was used to record cooling curves. The released heat can be related to the evolution of fraction solid using thermal analysis. Thermal analysis procedures are commonly based on Fourier’s law of heat conduction:

\[
c_v \frac{\partial T}{\partial t} = \nabla (k \nabla T) + \dot{q}_{sol}
\]

where \(c_v\) is the volumetric heat capacity, \(t\) is the time, \(T\) is the temperature, \(k\) is the thermal conductivity and \(\dot{q}_{sol}\) is a volumetric heat source, which corresponds to the release of latent heat during solidification. After rearranging and calculating \(\dot{q}_{sol}\) using the cooling curve and thermo-physical data (i.e. \(c_v\) and \(k\)) it is possible to calculate the latent heat and the evolution of fraction of solid. Two thermal analysis procedures are frequently used to do this; Newtonian thermal analysis, that uses a zero curve, based on the cooling curve prior to and after solidification. By subtracting the first derivative of the zero curve from the cooling curve it is possible to obtain an approximation of the heat evolved [46]. However, in this work Fourier thermal analysis will be used. This procedure requires at least two cooling curves measured in the solidifying melt, it is then possible to determine the Laplacian factor, \(\nabla^2 T\), in
the melt and it is possible to solve Equation 5 under the assumption that \( k \) is constant [47]. This procedure has the advantage that it takes into account the thermal gradient in the material, and it also enables the use of variable thermo-physical properties during solidification. The Fourier thermal analysis procedure used in this work was developed by Diószegi and Hattel [48].

Using the evolution of fraction of solid calculated with the thermal analysis procedure it is possible to obtain an expression for the radius of the growing eutectic cells using the Kolmogorov-Johnson-Mehl-Avrami (KJMA) expression for spherical cells [49-51]:

\[
f_s = 1 - \exp \left( -\frac{4\pi R_e^3 N_v}{3} \right)
\]

6.

Where \( f_s \) is the fraction solid, \( R_e \) is the radius of the eutectic cell and \( N_v \) is the number of growing cells. Rearranging and then differentiating Equation 6 the growth rate of the eutectic cell as a function of the fraction of solid can be obtained.

To be able to model the solidification of cast irons it is necessary to know the growth kinetics of the eutectic. Normally it is assumed that the growth is driven by the undercooling using the well known equation suggested by Oldfield [52]:

\[
\dot{R}_e = k_e \Delta T^n_e
\]

7.

Where \( k_e \) and \( n_e \) are constants characteristic of the material and \( \Delta T \) is the eutectic undercooling. The eutectic undercooling is calculated as the difference between the eutectic equilibrium temperature, \( T_{eq} \), and the temperature in the solidifying melt. To calculate \( T_{eq} \) it is necessary to account for segregation of alloying elements, which in this work was done using a Gulliver-Scheil equation along with data (e.g. distribution coefficients) obtained from Thermocalc [3]. The influence of the most important elements on \( T_{eq} \) was then calculated using a simplified phase diagram calculation [3]. Values for the growth rate originating from Equation 6 and values of the eutectic undercooling are then adjusted to Equation 7 and the values of \( k_e \) and \( n_e \) are calculated using a least square fit.

Graphs illustrating the entire process are shown in Figure 14, where the fraction solid and undercooling (Figure 14b and c) are obtained from the cooling curves (Figure 14a) for the low solidification rate sample from the Cu1-samples. The calculation of the dependence of the growth rate on the undercooling was done using all three cooling conditions (A, B and C described in Chapter 2.3.1) to obtain a relation that is valid for a wide span in cooling conditions. This is shown in Figure 14d, where the points from the three cooling rates at the fraction solid of 0.5 were plotted. The fraction solid of 0.5 was chosen to enable comparison with some literature sources concerning the growth rate in LGI [53, 54]. The constants, \( k_e \) and \( n_e \), included in Equation 7 were calculated from these results and \( k_e \) was found to be \( 1.19 \times 10^{-7} \text{ ms}^{-1} \text{K}^{-n_e} \) while \( n_e \) was 0.98. The constants were also calculated for a larger span in fraction solid (0.2 < \( f_s \) < 0.8), without significant change in the constants (\( k_e = 1.05 \times 10^{-7} \text{ ms}^{-1} \text{K}^{-n_e} \) and \( n_e = 0.98 \)).
SUMMARY OF RESULTS AND DISCUSSION

Figure 14: Graphs showing results from thermal analysis: a. Cooling curve and equilibrium temperature, b. fraction solid during solidification, c. undercooling as a function of fraction solid, d. growth rate of the eutectic as a function of undercooling.

Figure 15: The growth rates dependency on undercooling comparing CGI with LGI [53, 54].

Unfortunately no literature sources describing the growth rate of the eutectic in CGI could be found. However, a comparison with LGI is interesting since the two cast irons have many
similarities, specifically that the eutectic grows as spherical cells having sizes which are of the same order of magnitude. A comparison between the results found in this work and results from earlier research [53, 54] can be seen in Figure 15. The growth rate is approximately the same at low undercooling, while the growth in LGI is significantly more rapid at higher undercooling than in CGI. This is due to the quadratic dependence of the growth rate on undercooling proposed by Lux and Kurz [53], and Thorgrimsson [54] for all of the LGI except for Thorgrimsson’s flake graphite samples.

It should however be mentioned that due to differences in the thermal analysis method used some discrepancies seen in the results are likely to be due to error in the calculations and not due to kinetics of eutectic growth. The Fourier thermal analysis method was used in this thesis, while for the literature sources some form of Newtonian method was used. Furthermore, there are differences in the way the $T_{eq}$ was calculated. Specifically it appears as though the segregation, which will significantly affect the $T_{eq}$ and the undercooling was not accounted for.

![Figure 16: Colour etched microstructure showing variations caused by the different cooling conditions, generated by different mould material in the sampling cups. a. low solidification rate, b. intermediate solidification rate and c. high solidification rate.](image.png)

3.1.2 Formation of eutectic cells

The growth rate is one interesting aspect of the eutectic phase transformation, further aspects of this transformation were studied using the colour etching technique, described in Chapter 2.3.3. In Figure 16 the colour etched microstructure of the Cu2-samples (Table 1) is shown, for three different cooling conditions. The first obvious observation is the significant difference in coarseness of the structure. This was confirmed by the measurements seen in Table 2, where the low solidification rate samples generally have higher maximum eutectic cell sizes than the other samples.

<table>
<thead>
<tr>
<th>Solidification rate</th>
<th>Max eutectic cell size (µm)</th>
<th>Fraction eutectic CGI cells (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solidification rate</td>
<td>Low</td>
</tr>
<tr>
<td>Cu1</td>
<td>1660</td>
<td>1130</td>
</tr>
<tr>
<td>Cu2</td>
<td>1500</td>
<td>1330</td>
</tr>
<tr>
<td>Cu3</td>
<td>1500</td>
<td>1430</td>
</tr>
<tr>
<td>Cu4</td>
<td>1240</td>
<td>1130</td>
</tr>
</tbody>
</table>
Another observation that is possible to make from the photo micrographs is that eutectic cells in the low solidification rate samples appear to be more closely packed, meaning that there is less last to freeze areas between the eutectic cells. However, for the high solidification rate samples the cells almost appear to not impinge. This was quantified by measuring the area fraction of the clearly distinguishable eutectic cells; Table 2. The results showed a decreasing fraction of eutectic cells with increasing solidification rate. This can be related to the undercooling during the eutectic phase transformation.

Fras et al. [55] studied the undercooling during solidification for LGI and found two peaks in the undercooling curve. The first appears early during the solidification sequence, at the maximum in undercooling prior to recalescence and the second peak appears during the end part of solidification. They correlated the undercooling to nucleation and suggested that new eutectic grains nucleate continuously until the first maximum in undercooling is reached. During this period as the undercooling increased the critical size for a nucleus to become active decreased, meaning that smaller and smaller substrates were able to act as nuclei. As recalescence starts the undercooling will decrease so that to be an effective nucleus the substrates would have to be larger, however all larger substrates have already been activated prior to the maximum in undercooling and the nucleation stops. Nucleation starts again at a later stage of solidification when the undercooling reached at the first maximum is exceeded, giving rise to a secondary nucleation of eutectic grains [55].

The undercooling was evaluated for the Cu1-series, and the same trends as described by Fras et al. [55] were also found for CGI. That is to say an initial maximum prior to the recalescence and later a second maximum, or for the case of the lowest solidification rate a continuous increase in undercooling. Figure 17. In the figure the fraction solid at which the undercooling exceeds the undercooling at the first maximum is indicated with a circle. It can be seen that the position of this point depends on the solidification rate and that increasing solidification rate results in lower fraction of solid where secondary grains are able to nucleate. This suggests that secondary eutectic grains can nucleate and grow at an earlier stage than for the low solidification rate samples, thus at some point impeding the growth of the grains nucleated prior to the first maximum in undercooling. The trend concerning the fraction of eutectic CGI cells in Table 2 was related to the undercooling and it appears that due to the nucleation of the secondary grains the growth of the primary eutectic grains will be impeded,
resulting in an increasing fraction of eutectic CGI cells with lower solidification rates. This also means that the term “fraction of eutectic CGI cells” in Table 2 is a little misleading, and the term “fraction of primary nucleated eutectic CGI cells” would be more appropriate.

### 3.1.3 Nodule formation during solidification

According to the ISO-standard [10] an ideal CGI material only have graphite particles of a roundness shape factor lower than 0.525. However this is not compatible with production of components where a range of section thicknesses results in different cooling conditions and a range of nodularity. The increased nodularity manifests itself by a higher degree of roundness of the graphite and formation of graphite nodules. The formation of nodules will be discussed in this chapter. It is convenient to discuss nodules as they are the extreme case of the graphite shape, but in the following “nodules” should rather be interpreted as graphite particles of too high roundness shape factor, not only as graphite nodules per se.

![Figure 18: Colour etched sample showing graphite nodules in different parts of the microstructure, for the Cu2 sample with low solidification rate.](image)

When observing a normal CGI microstructure, e.g. Figure 4 and Figure 16, eutectic cells with compacted graphite particles are clearly seen and in between these cells graphite nodules are located. In Figure 18 nodules can be found in regions between the large eutectic cells with compacted graphite particles. Two different cases can be distinguished:

- **One rather large nodule is seen having a light blue colour surrounding the graphite, which implies that the material is high in Si and therefore has solidified at an early stage of the solidification sequence [14].** It is well known that higher nodularity is favored by high undercooling [22, 31] and this nodule nucleated early during the solidification sequence and then continued to grow and obtained its spherical shape during the period of time close to the first maximum in undercooling prior to recalescence. During this period the growth characteristic of SGI will appear, i.e. the nodule will be encapsulated by the austenite.

- **Nodules in Figure 18 can also be observed in light brown areas of the metal matrix, implying that they are formed during the later stages of solidification.** The nucleation of these nodules will coincide with what was previously described as secondary nucleation of eutectic cells, i.e. the late stage of solidification when the undercooling has exceeded the initial maximum before recalescence. At this stage the undercooling will be relatively high and there is an increased risk of high nodularity. An additional
reason for an increased nodularity is that Mg, which is the most common nodularising element used, segregates positively and thus will be enriched in these areas [13]. The common denodularising elements, O and S, also segregate to last to freeze areas, but these elements are commonly present in lower amounts, which would mean that the net result of the segregation will be an increase in nodularising elements [13].

Literature sources [31, 56] also show that an additional reason for increased nodularity is inoculation. The reason being that increasing amount of inoculant will decrease the maximum undercooling, and the solidification will in this way more closely resemble solidification in SGI, having a lower undercooling than CGI. This contradicts the previous discussion where it was stated that a high degree of undercooling induces higher nodularity. The explanation is that there are likely to be two different mechanisms responsible for the increased nodularity. The tendency to obtain increased nodularity for the case with high undercooling is fairly undisputed, and will not be further considered here.

The influence of inoculation on nodularity has not been clarified in the literature. One possible explanation may be related to the effect that the inoculating elements have on O and S. Normally inoculating elements tend to form sulphides and oxides [16, 17], implying that some of the denodularising elements will not be able to influence the graphite morphology during solidification and the material will obtain a higher nodularity. A possible solution to avoid excessive nodularity would be to add some S at the same time as the inoculation to neutralize the nodularising effect that the inoculant has. Sulphur has been used in a similar way to produce CGI from SGI melts, with good results [57].

### 3.2 ON THE WHITE SOLIDIFICATION OF CGI (SUPPLEMENTS II AND III)

If the temperature drops below the metastable eutectic temperature the white (carbide) eutectic is able to nucleate and grow. The white eutectic was studied using chill wedges. Both fracture surfaces and polished and etched structures of the wedges were studied. A typical fracture surface of the wedge can be seen in Figure 13b. Several areas of varying structure can be seen, and these were characterised and divided into four different zones that each had a distinct microstructure. These zones can be illustrated by observing the microstructure starting from the die wall at about half the wedge height and moving in towards the centre:

- **Zone 1**, shown in Figure 19a: This zone consists mainly of white eutectic radiating in from the die wall, however some dendrites can also be seen in this zone. Only small amounts of graphite can be seen and the graphite present is mainly found in the shape of graphite nodules. The main growth direction of the white eutectic is opposite to the direction of heat flow, perpendicular to the die wall. However, it is also seen that the white eutectic appears to have nucleated at relatively few places on the die wall, and consequently the structure grows in the typical fan-like manner described by Hillert and Subba Rao [33].

- **Zone 2**, shown in Figure 19b: The solidification rate will decrease closer to the centre of the wedge and depending on cooling conditions the white to grey transition will be found at some distance from the die wall. The transition structure found in this zone is mainly characterized by zone 1 structure on the white side and a fine graphite structure with high nodularity on the grey side. At the interface, small graphite nodules with austenite shells are found, and in between the small eutectic cells (in last to freeze areas) carbides growing perpendicularly to the die wall are found. Both in zone 1 and zone 2 it is seen that the prevalent graphite structure is nodules implying that during chill formation CGI is very similar to SGI.
Zone 3, shown in Figure 19c: in this zone the structure is completely grey (graphitic). The nodularity is still rather high and significant amounts of graphite nodules are found. However most of the graphite is present as CGI eutectic cells. As the cooling in this zone is still rather rapid there will be large numbers of eutectic cells and this appears to generate a rather even distribution of alloying elements (low segregation). As a result no segregation carbides form. Primary dendrites are clearly seen in Figure 19c, and the growth direction is evidently dependant on the die wall.

Zone 4, shown in Figure 19d: The most characterising feature of this zone is the relatively large CGI eutectic cells and the high fraction of white eutectic in the last to freeze areas. The white structure in these areas is commonly known as inverse chill. Inverse chill occurs due to a combination of segregation of carbide promoting elements and increased solidification rate. As the centreline areas are the last part of the wedge to solidify there is a limited release of latent heat from the surrounding material, giving higher solidification rate in this area which causes carbide formation close to the centreline.

Figure 19: Colour etched photo micrographs showing the different zones in the chill wedge. a. zone 1, b. zone 2, c. zone 3, d. zone 4.

3.2.1 Influence of alloying elements

The influence of alloying elements on the chill tendency of CGI was quantified by measuring two parameters on the fractured wedges: the length of the columnar zone 75 mm above the wedge tip; and the width of the wedge where it was judged that the columnar zones would intersect, Table 3. The results shown in the table are from one or two measurements.
depending on problems during the casting procedure. If two values were used an average was calculated and the span between the two values is given in parentheses. As the results are based on one or two measurements only their reliability results remains somewhat uncertain, but some general trends can be seen. Copper, silicon and tin all have a graphitizing effect on the material, with Cu having the most significant influence of the investigated elements. For the Si-samples it should be remembered that the C-content was decreased to retain a constant carbon equivalent as the Si-content was increased, which may explain the modest graphitizing influence of Si. For the Cem-series, which investigated the effect of carbide promoting elements, it was seen that Mo (which was increased in Cem4) influenced the chilling tendency to a larger extent than the other investigated elements (Cr, Mn).

<table>
<thead>
<tr>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>Cu1</th>
<th>Cu2</th>
<th>Cu3</th>
<th>Cu4</th>
<th>Si1</th>
<th>Si2</th>
<th>Si3</th>
<th>Si4</th>
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<tbody>
<tr>
<td>Width at columnar zone intersection</td>
<td>16.6</td>
<td>W</td>
<td>W</td>
<td>16.3</td>
<td>16.8</td>
<td>13.0</td>
<td>12.4</td>
<td>14.3</td>
<td>13.7</td>
<td>13.6</td>
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</tr>
<tr>
<td>Column. zone length at height 75 mm</td>
<td>5.5</td>
<td>W</td>
<td>W</td>
<td>6.5</td>
<td>4.3</td>
<td>3.8</td>
<td>3.3</td>
<td>5.4</td>
<td>5.3</td>
<td>1.6</td>
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The Si4-sample displayed a degenerate graphite morphology and the parameters given in Table 3 could not be measured. Furthermore measurements are missing for the two highest nodularity treatment level samples (T2 and T3). The reason that these samples could not be measured was because the fracture surfaces in these samples exhibited a completely white structure. This suggests that high nodularity CGI is more prone to chill formation than low nodularity CGI probably because close to the transition from grey to white the growth of the eutectic will influence the amount of white formed. If a material has higher nodularity the eutectic has to a large extent grown in a similar manner to SGI, meaning that the graphite, at an early stage, loses contact with the melt and the eutectic grows by diffusion through the surrounding austenite layer. Conversely, when a low nodularity CGI solidifies the graphite will remain in contact with the melt during a longer time, eutectic growth will be faster and more latent heat will be released preventing the temperature from dropping below the metastable transformation temperature. However, it is normally considered that CGI is more chill prone than SGI, in contrast to the above result. This is due to differences in inoculation between the different cast iron classes. In CGI inoculation must be limited in order avoid excessive nodularity, while no such limitations exists when producing SGI.
3.2.2 Simulation of white solidification

Simulations of the chill wedge were performed in a development version of the module MAGMAiron in MAGMAsoft [58] using models developed for the simulation of solidification of CGI. The simulation code uses deterministic models describing both the grey and white eutectic phase transformations. The models used for the growth of the grey eutectic have been described in a work by Fredriksson and Svensson [59]. The growth of the white eutectic was divided into two growth morphologies; columnar white (corresponds to zone 1 in the previous chapter) and segregation carbides (applies mainly to zone 4). The columnar white nucleates at the mould/die wall of the casting and grows in an opposite direction to the heat flow as long as the temperature is below the metastable eutectic temperature. The segregation carbides form as the segregation of alloying elements causes the metastable eutectic temperature to increase during the final part of the solidification sequence. This situation is visualised in Figure 6a.

The simulation software uses a finite difference method and the mesh used in the simulations consisted of cells that were on average 0.5 mm wide in the direction of the heat flow. To obtain realistic nucleation conditions for the simulations the “Inoculation method” was chosen to be “Good” and the “Treatment yield” was set to 4%, where “Inoculation method” and “Treatment yield” are standard input parameters in MAGMAiron. The cooling in the real casting was measured with thermocouples, as described in Chapter 2.3.2. These measurements were compared to simulated cooling curves and a temperature dependant heat
The transfer coefficient between the solidifying metal and the die was adjusted to obtain a good fit between the curves. This temperature dependant heat transfer coefficient was subsequently used in all of the simulations. The heat transfer coefficients between the die and the insulation material and the insulation material and the solidifying metal was given constant values of $300 \text{ Wm}^{-2}\text{K}^{-1}$ and $200 \text{ Wm}^{-2}\text{K}^{-1}$ respectively.

The simulations gave a qualitatively good agreement with the real casting, as seen in Figure 20. Both inverse chill (corresponding to zone 4) and columnar white (corresponding to zone 1) are present. The inverse chill can be seen as a 5-7 mm wide zone in the centre of the wedge extending upwards from where the columnar zones intersect. It is interesting to note that the simulations predict a slightly thinner inverse chill zone at approximately half the wedge height. This also appears to be the case in the real casting where inverse chill is slightly less pronounced around 60 mm above the wedge tip in Figure 20a. The accuracy of the simulations of the columnar zone lengths have been evaluated comparing simulations to the castings for the Cu-series. The columnar zone lengths of the real castings were quantified according to Chapter 2.3.3. In the simulations a percentage of white eutectic exceeding 35% was defined as white, this was based on comparisons between the fracture surfaces and the simulations, studying both inverse chill and the columnar white structure.

![Figure 21](image_url)

Figure 21: The influence of Cu on the length of the columnar white zone is evaluated using colour etched microstructure pictures, photographs of fracture surfaces and simulation results. a. 0.26 wt% Cu; b. 0.51 wt% Cu; c. 0.84 wt% Cu; d. 1.31 wt% Cu.
In accordance with the literature [5, 39] it is seen that increased Cu-content decreases the chill tendency of the material, resulting in a decreasing columnar zone, Figure 21. In the figure it can be seen that there is a disagreement between the different methods of empirically measuring the columnar zone, giving higher values of the columnar zone length for the photographs of the fracture surfaces than for the colour etched photo-micrographs. Bearing this in mind the accuracy of the simulations are good. The main discrepancy between simulations and the measurements is that the slope in the graphs concerning the simulations is less steep than the measured slope. Normally the columnar zone is dependent on the cooling conditions, and it is suggested that this might be the reason for the discrepancy. The cooling conditions can be altered in the simulations using the previously mentioned temperature dependent heat transfer coefficient, however this might not be enough to obtain a accurate description of the cooling conditions. The gap formation between the casting and the die caused by shrinkage during solidification, is not accurately simulated and will be a further source of error in the description of the cooling conditions.

3.3 ON THE SOLID STATE TRANSFORMATION IN CGI (SUPPLEMENTS IV, V AND VI)

Ferrite growth in cast irons is mainly controlled by carbon diffusion from the austenite to graphite particles which act as carbon sinks. Models for the ferrite growth already exist, especially for SGI but also for LGI [34, 60-62]. When developing a ferrite growth model for CGI it is valuable to consider growth models for other forms of cast irons. However as the growth involves diffusion of carbon to graphite particles of different morphology it is important to also study the differences originating from the graphite morphology.

3.3.1 Microstructure observations on ferrite growth

Compacted graphite particles grow in interconnected LGI-like eutectic cells, as depicted in Figure 22. However CGI is more similar to SGI than LGI when comparing the ferrite growth characteristics. This is evident in Figure 22a, where a ferrite layer has formed around a majority of the graphite particles. This suggests that the ferrite growth can be modelled using SGI models modified to take the different graphite geometry into account.

Figure 22: a. Ferrite forms a layer enveloping the graphite. b. Ferrite grows in areas rich in ferrite promoters and depleted of pearlite promoters.
It is clear from the microstructure images that ferrite is preferentially located in certain areas of the microstructure, while other areas appear to be predominantly pearlitic. This is not due to the lack of graphite particles on which ferrite can grow, but rather a consequence of the segregation of alloying elements. Pearlite promoters are commonly rejected by the solidifying material and will thus be present in larger amounts in the last to solidify areas (positive segregation) in the microstructure, while Si which is an important ferrite promoting element is preferentially dissolved in the solid (negative segregation). This creates an inhomogeneous distribution of ferrite.

In CGI material of higher nodularity, ferrite around graphite nodules can be seen in areas between the larger ferrite agglomerates. Using colour etching techniques the segregation pattern of the material can be revealed. Judging from the segregation pattern it was seen that these nodules have solidified early in the solidification sequence, as discussed in Chapter 3.1.3. Thus, the material surrounding the graphite nodules had a similar composition as the larger ferrite agglomerates, which also solidified early during the solidification sequence.

### 3.3.2 Discretisation into layers

The segregation of alloying elements will influence both nucleation and growth of ferrite. Due to segregation it is appropriate to divide the eutectic cell into spherical layers (similar to the layers of an onion), Figure 23. The size of the eutectic cells has been evaluated using image analysis. If it is assumed that the centre of the eutectic cells solidifies first and the most remote layer solidifies last, then the segregation of all relevant alloying elements can be modelled using the Gulliver-Scheil equation. The local alloy content is then used to calculate the start temperatures for ferrite and pearlite formation in each layer. Equations for the start temperatures for ferrite and pearlite formation were obtained from work done by Wessén [63] and Lacaze [64].

The use of Scheil segregation in combination with the start temperature equations gives a significantly larger temperature range between the start of ferrite growth and pearlite growth in the cell centre than in the most remote layer. This means that ferrite formation will be favoured in the cell centre, with an increasing tendency towards pearlite formation when moving away from the eutectic cell centre.

![Figure 23: A eutectic cell divided into layers and the graphite geometry used for the model.](image)

### 3.3.3 Ferrite growth rate

When the temperature decreases below the ferrite transformation temperature, ferrite is able to nucleate. The ferrite growth will mainly occur around graphite particles as shown in Figure 22. It is consequently reasonable to say that the ferrite mainly nucleates on the graphite
particles. Ferrite growth is assumed to be governed by the diffusion of carbon atoms to the graphite particles, and it is therefore important to have a good description of the graphite geometry. The graphite within a CGI eutectic is a complex interconnected network of different graphite shapes, making it difficult to obtain a good description of the graphite geometry. It is necessary to make simplifications regarding the geometry, and in the current model a simple cylindrical disc was used according to Figure 23. The cylindrical disc was chosen because a two-dimensional section through a volume of randomly oriented cylindrical discs will resemble the microstructure observed in CGI. The parameters needed to describe the cylindrical disc can be seen in Figure 23. Furthermore the number of particles needs to be known. The necessary parameters have been evaluated from image analysis of microstructure pictures.

The nucleation of ferrite is simplified in the current model and simulated by allowing the ferrite to grow at a reduced rate during the initial stage of ferrite growth. A model for ferrite growth in SGI developed by Wessén and Svensson [34] is used to obtain the growth rate. In the model for SGI the ferrite growth following the nucleation event is divided into two steps:

During the first step an interface reaction at the graphite/ferrite interface determines the growth rate. Specifically the amount of carbon that can be added to graphite is the governing factor. In order to calculate this, the interface coefficient, \( \mu \), needs to be evaluated. This was done using a thermal analysis procedure developed for SGI.

During the second stage the growth rate is controlled by diffusion of carbon through the ferrite layer surrounding the graphite. The second step is very much in line with previous work in the field [60, 61].

For the case of CGI it is reasonable to assume that the first step will be the dominating growth mechanism. The explanation for this is partly that the graphite in CGI is less inclined to absorb carbon atoms during growth than in SGI, and partly that compacted graphite particles have larger surface area to volume ratios than graphite nodules. Considering this, the interface controlled first step is assumed to be the controlling mechanism when modelling ferrite growth in CGI.

In the work by Wessén and Svensson [34] a carbon mass balance at the graphite/ferrite interface was used to obtain the equation governing the growth rate. This equation was modified to conform to the difference in graphite geometry:

\[
\frac{dY_a}{dt} = \left( \frac{C_{\alpha}^{\alpha} - C_{\alpha}^{gr}}{C_{\alpha}^{gr/a} - C_{\alpha}^{gr/y}} \right) \mu \exp \left[ \pi r_y^2 n_y \left( 2Y_a + t_{gr} \right) \right]
\]

Where \( dY_a/dt \) is growth rate of the ferrite, \( C_{\alpha}^{\alpha} \) is the non-equilibrium carbon content at the graphite/ferrite interface resulting from the sluggishness of the interface reaction, \( \mu \) is an interface coefficient depending on the temperature and alloy content, \( n_y \) is the number of graphite particles per volume. The remainder of the parameters can be found in Figure 7 and Figure 23. As mentioned previously, the interface coefficient \( \mu \) needs to be evaluated by thermal analysis. In the current study a thermal analysis procedure developed for SGI was used as a first approximation.

Simulations were performed using the above model. The results showed a qualitative agreement with a real microstructure, i.e. the cell centres were enriched with ferrite, while the outer layers were mainly pearlitic. When comparing the simulated ferrite content with the measured ferrite content from a samples cast in the sampling cup it was clear that there was
some inconsistency between the simulation and the cast sample. Discrepancies in the simulated cooling curves were also found, giving a significantly higher growth temperature in the simulated curves. The disagreement between simulations and real samples was attributed to the simplified nucleation used in the model and that the interface coefficient was evaluated using a thermal analysis procedure developed for SGI and not CGI. This shows that the model is not complete, but the initial results are qualitatively in agreement with microstructural observations.

3.4 INFLUENCE OF ALLOYING ELEMENTS AND MICROSTRUCTURE ON MECHANICAL PROPERTIES (SUPPLEMENTS V, VI AND VII)

Previously in this chapter the mechanisms leading to microstructure formation in CGI have been covered. This part focuses on discussing the influence of alloying elements on microstructure formation and tensile properties and presents results from tensile tests and from the thermal analysis cup.

In Table 1, the chemical compositions of the different trials are given. In each of the trials one alloying parameter was varied to study the affect of that parameter on microstructure and mechanical properties. The parameters changed were:

- Treatment level (T); the nodularity was changed by adding different amounts of Mg. Three levels were studied (0.006; 0.013; and 0.020 wt% Mg).
- Copper (Cu); four levels were studied (0.26; 0.51; 0.84 and 1.31 wt% Cu).
- Silicon (Si); four levels were studied (1.89; 2.31; 2.96 and 3.85 wt% Si). The carbon content was adjusted to obtain a constant carbon equivalent.
- Tin (Sn); four levels were studied (0.015; 0.032; 0.060 and 0.095 wt% Sn).
- Carbide promoter additions (Cem); four levels were studied. To provoke carbide formation Mn, Cr and Mo additions were made (various amounts, Table 1).

3.4.1 Influence of treatment level (T)

The nodularising treatment levels were altered, which resulted in a varying graphite morphology in the material. The influence of Mg (0.006 to 0.020 wt%) on the nodularity is well known from its usage for both SGI and CGI. However it is interesting to see if there are other effects of the increased nodularity.

The effect on the nodularity is in agreement with common knowledge (Table 4), i.e. the nodularity increases with increasing treatment level as well as with increasing cooling rate. Not only the nodularity, but also the size and distribution of the graphite were affected by both the treatment level and the cooling rate. The graphite fraction measured by image analysis was similar in all samples, implying that there were either few large graphite particles or many small and well distributed particles. The cooling rate had the greatest influence with substantially more graphite particles in the ‘high’ and ‘intermediate’ solidification rate samples than in the ‘low’ solidification rate samples. This will affect the solid state transformation, as explained in Chapter 1.3.2. While the lowest solidification rate means that ferrite will be able to grow during a long period of time, the relatively few graphite particles limit ferrite growth to only a few locations in the structure. This resulted generally in more pearlite in the ‘low’ solidification rate samples than in ‘high’ and ‘intermediate’ solidification rate samples. It is also interesting to note that in these experiments an increase in nodularity caused an increase in pearlite content, i.e. T3 had higher pearlite content than T1, Table 4.
Table 4: Results from the sampling cups and the tensile tests for the T, Cu and Si series. Tensile tests were performed using 2 to 4 bars/test variant, with the results for ultimate tensile strength given as the average value with the span of the UTS given in parentheses.

<table>
<thead>
<tr>
<th>Sol. rate</th>
<th>Thermal analysis cup</th>
<th>Tensile tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nodularity (%)</td>
<td>2.5/62.5 Nodularity (%)</td>
</tr>
<tr>
<td></td>
<td>Pearlite content (%)</td>
<td>UTS (MPA) Average (span)</td>
</tr>
<tr>
<td>Low</td>
<td>7.1</td>
<td>307 (9)</td>
</tr>
<tr>
<td>T1</td>
<td>9.3</td>
<td>323 (4)</td>
</tr>
<tr>
<td>High</td>
<td>10.4</td>
<td>380 (15)</td>
</tr>
<tr>
<td>Low</td>
<td>9.9</td>
<td>438 (6)</td>
</tr>
<tr>
<td>T2</td>
<td>11.6</td>
<td>462 (7)</td>
</tr>
<tr>
<td>High</td>
<td>15.9</td>
<td>513 (14)</td>
</tr>
<tr>
<td>Low</td>
<td>30.8</td>
<td>498 (6)</td>
</tr>
<tr>
<td>T3</td>
<td>29.4</td>
<td>522 (-)</td>
</tr>
<tr>
<td>High</td>
<td>33.8</td>
<td>608 (15)</td>
</tr>
<tr>
<td>Low</td>
<td>5.1</td>
<td>299 (6)</td>
</tr>
<tr>
<td>Cu1</td>
<td>4.0</td>
<td>309 (1)</td>
</tr>
<tr>
<td>High</td>
<td>10.7</td>
<td>347 (9)</td>
</tr>
<tr>
<td>Low</td>
<td>6.1</td>
<td>353 (22)</td>
</tr>
<tr>
<td>Cu2</td>
<td>7.4</td>
<td>354 (2)</td>
</tr>
<tr>
<td>High</td>
<td>12.0</td>
<td>378 (6)</td>
</tr>
<tr>
<td>Low</td>
<td>5.3</td>
<td>404 (1)</td>
</tr>
<tr>
<td>Cu3</td>
<td>6.3</td>
<td>424 (2)</td>
</tr>
<tr>
<td>High</td>
<td>12.3</td>
<td>450 (26)</td>
</tr>
<tr>
<td>Low</td>
<td>10.3</td>
<td>387 (13)</td>
</tr>
<tr>
<td>Cu4</td>
<td>11.9</td>
<td>406 (3)</td>
</tr>
<tr>
<td>High</td>
<td>16.5</td>
<td>439 (14)</td>
</tr>
<tr>
<td>Low</td>
<td>11.3</td>
<td>426 (5)</td>
</tr>
<tr>
<td>Si1</td>
<td>12.8</td>
<td>452 (5)</td>
</tr>
<tr>
<td>High</td>
<td>18.5</td>
<td>510 (5)</td>
</tr>
<tr>
<td>Low</td>
<td>7.9</td>
<td>412 (1)</td>
</tr>
<tr>
<td>Si2</td>
<td>9.4</td>
<td>431 (0)</td>
</tr>
<tr>
<td>High</td>
<td>10.4</td>
<td>377 (11)</td>
</tr>
<tr>
<td>Low</td>
<td>10.1</td>
<td>413 (5)</td>
</tr>
<tr>
<td>Si3</td>
<td>13.0</td>
<td>439 (1)</td>
</tr>
<tr>
<td>High</td>
<td>13.0</td>
<td>429 (45)</td>
</tr>
<tr>
<td>Low</td>
<td>8.7</td>
<td>353 (15)</td>
</tr>
<tr>
<td>Si4</td>
<td>13.8</td>
<td>371 (1)</td>
</tr>
<tr>
<td>High</td>
<td>17.4</td>
<td>391 (2)</td>
</tr>
</tbody>
</table>
This can be explained by the higher surface area/volume ratio of low nodularity graphite particles compared to CGI with higher nodularity, where the graphite generally is rounder. The higher pearlite content seen in T3 implies that CGI is more prone to ferrite formation than SGI, indicating that CGI is not intermediate between LGI and SGI in this respect. The increase in nodularity in combination with the increased pearlite content resulted in a nearly linear relation between the mechanical properties and the Mg-level, Table 4. The T2-samples showed higher mechanical properties than T1 mainly due to a higher pearlite content, while the T3 samples showed the highest properties due to the combination of high nodularity and high pearlite content.

### 3.4.2 Influence of Copper (Cu)

Copper promotes pearlite in cast irons; in the experiments performed this resulted in a gradual increase in pearlite content, for an increase in Cu from 0.26 to 1.31 wt%. The higher pearlite content generally caused an increase in mechanical properties, Table 4. Although the increase in Cu generally resulted in better mechanical properties, the highest Cu-content samples were accompanied by a slight decrease in tensile strength. As Cu causes a solid solution strengthening effect in cast irons, the decrease in tensile strength might be an effect of matrix embrittlement [65]. The decrease in tensile strength in combination with the fact that Cu did not promote a completely pearlitic matrix (71-95%, depending on cooling conditions) indicates that Cu should not be used as pearlite promoter alone. When a fully pearlitic matrix is desired then Cu in combination with another pearlite promoter, e.g. Sn or Cr, is recommended.

It was also seen that Cu has an influence on the graphite morphology, as the nodularity increased with an increasing Cu-content in the sampling cups. This influence of Cu, previously pointed out by Popov and Sizov [66], was especially pronounced for Cu-contents above 1 wt%.

### 3.4.3 Influence of Silicon (Si)

Silicon (Si) is added mainly for its strong graphitising effect. The Si-content was varied between 1.89 and 3.85 wt%. The graphitising effect of Si was clearly seen in the chill wedges. However the graphitising effect in the thermal analysis cup and the tensile tests could not be verified, because the microstructure of these samples was generally free from carbides. The amount of carbides was not quantified, but it was judged to be less than 1 %. The carbides were generally of intercellular type, indicating that they formed late during solidification as a consequence of segregation.

An inoculation effect was seen in the sampling cups as the Si-content was increased. The amount of graphite particles, evaluated by image analysis increased significantly with increasing Si-content, as well as with increasing cooling rate. This resulted in an increased nodularity of up to 10%, depending on cooling rate when the Si-content increased from 2.31 wt% to 3.85 wt%, Table 4.

During the solid state transformation Si promotes ferrite by expanding the difference between the stable and metastable eutectoid temperatures. The raised stable eutectoid temperature was observed in the cooling curves for the Si samples, Figure 24. Using Newtonian thermal analysis the fraction transformed austenite could be evaluated, giving a clearer understanding of the start temperatures for ferrite growth, Figure 25.

By means of image analysis the ferrite promoting effect of Si could be studied. The matrix changed from mainly pearlitic to mainly ferritic with the increase in Si-content. This had a detrimental effect on strength properties, with a decrease in ultimate tensile strength.
corresponding to the decrease in pearlite content, Table 4. It is commonly expected that the hardness of the material is a function of the pearlite content, however the highest Si content samples deviated from this trend which can be seen in Figure 26, showing the relation between pearlite content and hardness for all samples in the experimental series. In the figure the highest Si content sample are the three samples that have a pearlite content of around 20%, but still have Brinell hardeneses of about 190. This was attributed to the solution hardening effect that Si has on ferrite [67].

3.4.4 Influence of Tin (Sn)

Similar to copper, tin has a pearlite promoting effect in cast iron. Sn was added in the amounts of 0.015 up to 0.095 wt%. The assumed mechanism for the pearlite promoting effect is also similar, i.e. Sn creates a thin layer around the graphite which inhibits the carbon
SUMMARY OF RESULTS AND DISCUSSION

diffusion that enables ferrite growth \([40, 41]\). Furthermore it was also observed that Sn has an influence on the graphite morphology of the material. For the castings from the sampling cup a decrease in nodularity was evident for an increase in Sn-content from 0.015 to 0.06 wt\%. This can be explained by the effect that Sn has on the thin liquid channels associated with CGI \([21, 29]\). Sn segregates to the last to solidify areas where it lowers the liquidus temperature; and this is said to cause thin liquid channels to form. The decreased nodularity did, however, not affect the mechanical properties in a major way. It is clear from **Table 5** that the pearlite content has a greater influence on mechanical properties than the nodularity for the Sn-trials. Interestingly, Sn also seemed to affect the size and distribution of the graphite. In the sampling cups the graphite particle density, i.e. the number of graphite particles in the polished plane, increased with the Sn-content. As the analysis of graphite

| Table 5: Results from the sampling cups and the tensile tests for the Sn and Cem series. Tensile tests were performed using 2 to 4 bars/test variant, with the results for ultimate tensile strength given as the average value with the span of the UTS given in parentheses. |
|----------------|----------------|----------------|----------------|----------------|
| Sol. rate      | Thermal analysis cup | Tensile tests |
|                | Nodularity  | Pearlite content | UTS (MPA) | HBN 2.5/62.5 |
|                | (%)         | (%)             | Average (span) | (%)            |
| Sn1            | Low         | 8.3 56         | 303 (3) | 135 8.1 30 |
|                | Interm.     | 9.2 49         | 311 (-) | 140 6.2 29 |
|                | High        | 11.8 58        | 381 (14) | 174 13.4 46 |
| Sn2            | Low         | 6.9 76         | 308 (3) | 174 4.7 50 |
|                | Interm.     | 8.1 61         | 323 (1) | 169 5.0 57 |
|                | High        | 9.5 65         | 355 (2) | 174 4.4 52 |
| Sn3            | Low         | 6.5 93         | 401 (8) | 191 6.4 81 |
|                | Interm.     | 6.4 80         | 422 (2) | 204 7.6 82 |
|                | High        | 6.5 77         | 420 (5) | 208 6.0 80 |
| Sn4            | Low         | 6.9 97         | 423 (3) | 211 4.3 80 |
|                | Interm.     | 8.0 95         | 449 (6) | 218 4.7 81 |
|                | High        | 6.8 96         | 470 (28) | 225 3.9 90 |
| Cem1           | Low         | 13.0 98        | 451 (8) | 204 11.6 84 |
|                | Interm.     | 11.5 93        | 474 (6) | 211 14.4 84 |
|                | High        | 16.4 92        | 505 (3) | 218 9.5 84 |
| Cem2           | Low         | 8.8 96         | 448 (3) | 211 16.7 86 |
|                | Interm.     | 12.2 91        | 474 (4) | 211 6.8 85 |
|                | High        | 17.0 92        | 502 (14) | 218 10.2 82 |
| Cem3           | Low         | 6.7 96         | 418 (11) | 211 6.1 87 |
|                | Interm.     | 8.6 92         | 450 (4) | 211 7.6 87 |
|                | High        | 11.3 92        | 491 (3) | 222 6.6 83 |
| Cem4           | Low         | 11.3 96        | 458 (55) | 211 26.5 84 |
|                | Interm.     | 10.0 96        | 487 (15) | 218 17.2 88 |
|                | High        | 12.7 94        | 533 (3) | 224 8.7 89 |
particle density concerns the polished plane of the sample there are two possible explanations for this increase; either the number of graphite particles increased due to increased number of eutectic cells, or the graphite branched and twisted indicating a change in the graphite growth morphology, resulting in an increased risk of counting the same graphite particle several times during image analysis.

3.4.5 Influence of Carbide promoters (Cem)

Similar to the Si experiments, no significant amount of carbides was found in the microstructure of the carbide promoter experiments. Some intercellular carbides were found, but a clear increase in the amounts of carbides could not be confirmed when increasing the carbide promoter additions. No chill formation at the mould walls could be seen, indicating that the carbide promoters were not potent enough, or that the cooling rates were too low to promote chill, for either the sampling cup or the tensile test bars. Further indications that the carbide content was approximately the same in the carbide promoter experiments as in the other experiments is that the hardness of these samples can be correlated to the pearlite content, Figure 26. The pearlite content was consistently high in the carbide promoter experiment samples. This resulted in generally high and similar tensile properties and hardness, Table 5. However the increased Mo-content affected the properties and resulted in a significant increase in UTS. According to the literature this might be explained by the refining effect that Mo has on pearlite lamellar spacing [68]. The lamellar spacing was investigated using a scanning electron microscope. It was clear that cooling rate had an influence on the lamellar spacing, which also is seen in the mechanical properties. However no clear indication of a decreased lamellar spacing due to an increase in Mo-content could be observed.
This work has discussed matters concerning microstructure formation during solidification and solid state transformation in CGI. The three generic levels; ‘characterise’, ‘understand’ and ‘model’ set forth in the research approach have been guiding in the work. Of these guidelines, ‘understand’ has been the most important and the focus of this chapter is to highlight some issues that have improved the understanding of microstructure formation in CGI. A common theme of the thesis has been to follow the material from melt through solidification and solid state transformation and to discuss issues of interest along the way. This theme will also be utilized in the following summary.

Several phenomena related to the grey solidification of CGI have been discussed, mainly aspects related to the eutectic growth. The growth rate of eutectic cells was evaluated using Fourier thermal analysis. The growth rate was seen to depend linearly on the eutectic undercooling. CGI was compared to LGI and it was seen that the growth rate is approximately the same at low undercooling, while the growth rate in LGI was superior at higher undercooling. Studying the undercooling during the solidification sequence in combination with colour etched photo-micrographs it was seen that the eutectic nucleates on two separate occasions. This was correlated to the solidification rate and it was seen that samples with high solidification rate exhibited low amounts of eutectic cells that nucleated early during solidification. In a normal CGI casting not only eutectic cells of low nodularity are present but also, depending on cooling conditions and alloying content there are commonly graphite nodules found in the microstructure. Nodules found in the structure were found to have solidified either early or late during solidification. The nodule formation early and late during the solidification sequence was correlated to higher undercooling during these stages of the solidification sequence and segregation of nodularising elements for the case of nodules formed late.

If the temperature drops below the metastable eutectic temperature before the material has solidified the white eutectic is able to grow. The microstructure was investigated on chill wedges and it was seen that the microstructure could be characterised in terms of four zones. In the first zone situated closest to the die wall, a predominantly white structure was found. The second zone, adjacent to the first, consists of a transitional structure from white to grey. In the third zone a completely grey structure is found. In the fourth zone, situated in the centre of the wedge, a mottled structure was seen, consisting of coarse grey eutectic cells and inverse chill. The nodularity in the first two zones is very high and the graphite morphology
resembles SGI more than CGI, suggesting that chill formation in CGI is closely related to SGI. Some differences regarding chill formation between SGI and CGI were however seen. Generally it is not possible to inoculate a CGI melt to the same extent as a SGI melt due to the risk of increased nodularity associated with inoculation in CGI. However, if two CGI melts of equal nucleation potential are compared, the melt with higher nodularity is likely to have higher chill tendency due to the lower growth rate of a graphite eutectic with higher nodularity.

The chill formation in the chill wedges was simulated and good agreement between the simulations and the real castings was found. Generally good agreement between experiments and simulation was found regarding both the columnar white formation and the inverse chill formation.

After completed solidification the temperature will decrease and at about 738°C the solid state transformation will start. The phase transformation from austenite to ferrite and graphite has been studied in this work and a model for the ferrite growth was developed. There has not been an extensive amount of research performed regarding modelling of microstructure formation in CGI. Some models describing the solidification have been published, while no publications, to the knowledge of the author, regarding the solid state transformation has been published prior to the model described in this thesis. The model assumes that the growth rate of ferrite is controlled by an interface reaction at the ferrite/graphite interface. The segregation of alloying elements is accounted for using the Gulliver-Scheil equation. Cylindrical discs were used to model the geometry of the graphite particles in CGI. Results from simulations using the model show a good qualitative agreement with microstructural observations, however some discrepancies were found so that further improvement is still needed.

The influence of alloying elements on microstructure formation and mechanical properties was also investigated. Generally the influence of the investigated alloying elements agree with results found in LGI and SGI. It was seen that Mg promote a higher nodularity in CGI and that high nodularity CGI is more prone to pearlite formation than low nodularity CGI. This results in increasing mechanical properties with higher Mg content, depending on both increased nodularity and increased pearlite content. Cu and Sn promote pearlite, which will increase the tensile strength of the material. It was also seen that the chilling tendency was reduced due to increasing amounts of Cu and Sn. Si promotes ferrite, thus lowering the tensile strength of the material. Similarly to Cu and Sn, Si had a graphitising effect, meaning that the chilling tendency was decreased as the Si content increased. Furthermore it was seen that Si strengthens the ferrite by solution hardening. The influence of carbide promoting elements (Cr, Mn, Mo) was studied. No significant amount of carbides was found in the samples having moderate solidification rates, i.e. the sampling cup and the tensile test bars. In the chill wedge it was seen that chill increased as the carbide promoter content increased, and especially Mo caused an increase in chill tendency. The tensile strength of these samples was relatively high, mainly due to the high pearlite content obtained.
CHAPTER 5

FUTURE WORK

CHAPTER INTRODUCTION

Research regarding CGI will intensify as the significance for industrial applications continues to increase. During the course of this work some issues were encountered that were not clear, or not sufficiently researched. It is the hope of the author that some of these issues will be found interesting enough to perform further research, or perhaps interesting enough to invest the time and effort required to write another doctoral thesis.

Microstructure formation in CGI has been studied from several different angles in this work. However, although some issues were investigated and explained, numerous interesting questions remain unanswered, a few of which are summarised below.

Research regarding the precipitation of the primary austenite has not been the focus of this work, but nevertheless it is an important part of solidification that also influences the eutectic transformation. In a study by Rivera et al. it was seen that primary austenite grains in CGI are substantially smaller than primary austenite grains in both LGI and SGI. The reason for this is not clear. Related to this is the start of the eutectic reaction, specifically how the primary austenite dendrite network affects the start of the eutectic reaction would be an interesting research topic.

During the eutectic reaction the most obvious difficulty from an industrial point of view is to control the graphite morphology. One aspect that has been touched upon in this thesis is the influence of inoculation on the nodularity. It is somewhat puzzling that low undercooling caused by inoculation induces higher nodularity, while at the same time high undercooling caused by thin sections induces higher nodularity. In this work it is suggested that there are two separate reasons for this, of which one mentioned is that inoculation deoxidizes and/or reduces the sulphur content in the melt, which results in an increased nodularity. This could be investigated using oxygen activity measurements, i.e. measure oxygen activity and see what happens when inoculation is performed on a melt. A study performed by Mampaey et al. showed a clear correlation between oxygen activity and nodularity, indicating that the influence inoculation has on oxygen activity could be measured and its influence on the nodularity investigated.

It is the opinion of the author, that to further deepen the knowledge concerning the different growth morphologies of the different graphitic cast irons, the surface energy during solidification should be studied, and care should be taken to study how the surface energies affect the growth rates of the eutectic.

The model developed in this work concerning the solid state transformation still requires some work. One topic that was not sufficiently dealt with is the nucleation of the ferrite on
the graphite. In order to develop a nucleation law specifically for CGI thermal analysis along with quenching experiments at various stages of the transformation is suggested. The model could also benefit from a careful examination of the currently used graphite and ferrite geometry, to ensure that the predictions of the ferrite growth are precise. The interface coefficient $\mu$ used to describe the carbon absorption at the graphite/ferrite interface was developed for the case of SGI. Some work is required to develop a procedure that accommodates the difference in geometry found in CGI compared to SGI. Finally after these alterations have been performed it is suggested that the models should be validated using a new geometry.
REFERENCES

APPENDED PAPERS


Supplement VIII – M. König (2009): “Compilation of Results Regarding the Influence of Alloying Elements on Microstructure and Mechanical Properties of CGI”, A collection of results from experiments performed within the OPTIMA-CGI project.