

Influence of Cooling Rate on Nature and Morphology of Inter cellular Precipitates in Si-Mo Ductile Irons

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Abstract. This work is designed to better understand the influence of cooling rate on the nature and morphology of inter cellular precipitates in Silicon-Molybdenum ferritic ductile iron (SiMo). Plates of 3, 6, 9 mm thickness were cast in greensand and investment casting molds to give a wide spectrum of cooling rates. It was found that at higher cooling rates, the inter cellular regions have a lamellar structure typical of pearlite. With decreasing cooling rates, the precipitate contains complex (Fe-Mo-Si) carbides of fine spheroidal or rod-like structure surrounding the eutectic carbides.

Intensive Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) and Optical Microscopy (OM) investigations showed that the eutectic carbides are mainly (Fe, Mo, Si) C containing up to 48% Mo, whereas the fine precipitates contain lower Mo-contents. Both carbide types did not show to have a strict stoichiometric composition. The solidification and solid-state transformation path was determined using both phase diagram calculated from Thermo-Calc software as well as Differential Scanning Calorimetry (DSC).

Introduction

Over the past few decades, SiMo ductile irons have been finding increasing applications for high temperature automotive components such as exhaust manifolds and turbocharger housings [1-3]. The oxidation resistance, high temperature strength and dimensional stability are required to cope with the increasingly higher temperature internal combustion exhaust gases (may reach up to 880°C) associated with improving the Internal Combustion Engine (ICE) efficiency [4-6]. There are material specifications typically impose limits on pearlite content in ferritic ductile irons to avoid the alloy dilation and growth associated with decomposition of the pearlite cementite at high operation temperatures [2]. SiMo ductile irons have an advantage over high – Si ductile iron containing pearlite and the presence of a Fe₂MoC/M₆C type carbide phases with higher thermal stability, leads to remarkable dimensional stability up to 925°C [2].

Casting experiments and solidification modeling have shown, that the shrinkage tendency of high Si-Mo containing 4-6% Mo can be controlled in the same level as that of regular SiMo, using suitable C.E (4.35-4.85), depending upon the critical thickness of the casting [3].

The impact of the section thickness and cooling rate of the castings on the cell boundary carbide precipitation in SiMo alloys has been scarcely dealt with in the literature. There is a need to better understand the nature and morphology of inter cellular precipitates in SiMo ductile iron. The main objectives of this work, therefore, is to investigate the influence of the cooling rate of thin-wall SiMo castings of section thickness ranging from 3-9 mm and cast in greensand or investment casting molds.

Experimental Procedure

Samples Preparation

Melting of the experimental heats was carried out in a medium frequency (1000 Hz) acid lined induction furnace of 100 kg capacity. The metallic charge used to prepare the base molten iron consisted of high purity (Sorel) pig iron, steel scrap, ferrosilicon 75%, Ferro-molybdenum 60% as well as carburizing material. The molten iron was tapped at 1500°C, then treated with 1.4% of Mg-FeSi spheroidizing alloy containing 9-10% Mg and inoculated with (1.2-2%Ce) inoculant.

The pattern was used to cast 200×150 mm plates with thickness of 3, 6 and 9 mm. The chemical composition of the SiMo ductile iron samples poured is as follows, in wt. percent: C: 2.61%, Si: 5.07%, Mo: 0.7%, Mn: 0.26%, P: 0.035%, S: 0.012%, Mg: 0.037%.

Metallographic Investigation

Metallographic examinations were carried out on samples, etched with 2% Nital. OM at high resolution and SEM FEI-QuantaTM was used for further investigation and analysis of eutectic carbides and the fine precipitate phases formed in the vicinity of the cell boundaries.

Solidification and Solid-State Transformation Path

The Fe-Mo-C phase diagram of the alloy investigated throughout this work (Si: 5 and Mo: 0.7) was calculated using “Thermo-Calc 2017a” data base: TCFE 8-V8.1 and the volume fraction of phases as well as transformation temperatures were calculated.

However, for more accurate determination of the phase transformation temperatures, the data obtained from the calculated phase diagram were compared to those measured using the Differential Scanning Calorimetry (DSC). Throughout this investigation, Differential Scanning Calorimeter NETSCH STA 409 C/CD was used, with cooling rate of 30°C/min.

Results & Discussions

Solidification and Solid-State Transformation Sequence

Thermo-Calc phase diagram of 0.7% Mo section of the Fe-Mo-C is shown in fig (1-a,b), which illustrates the formation of carbide phases in equilibrium with austenite (FCC) and ferrite (BCC) on cooling from the liquidus line (~1270°C) to the room temperature.

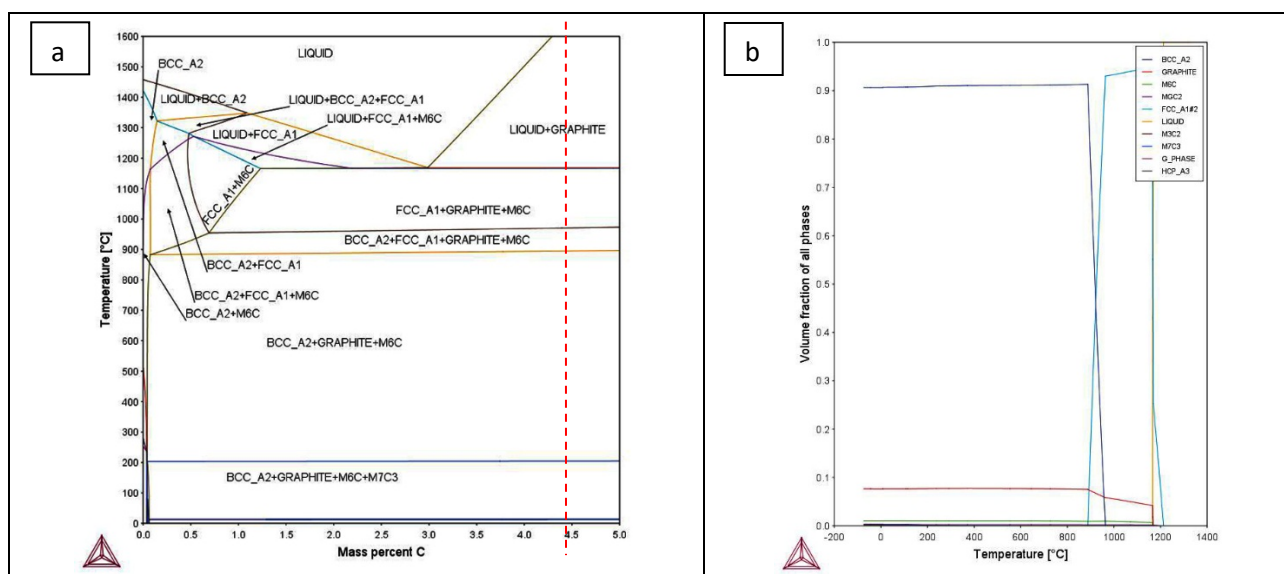


Fig 1: (a) Thermo-Calc phase diagram of SiMo (the dashed line represent the C.E of produced alloy≈4.3), (b) volume fraction of all phases formed

Figure (2) shows DSC curve illustrating the sequence of phase transformations during cooling at 30°C/min of a SiMo sample cast in 3-mm thick plates.

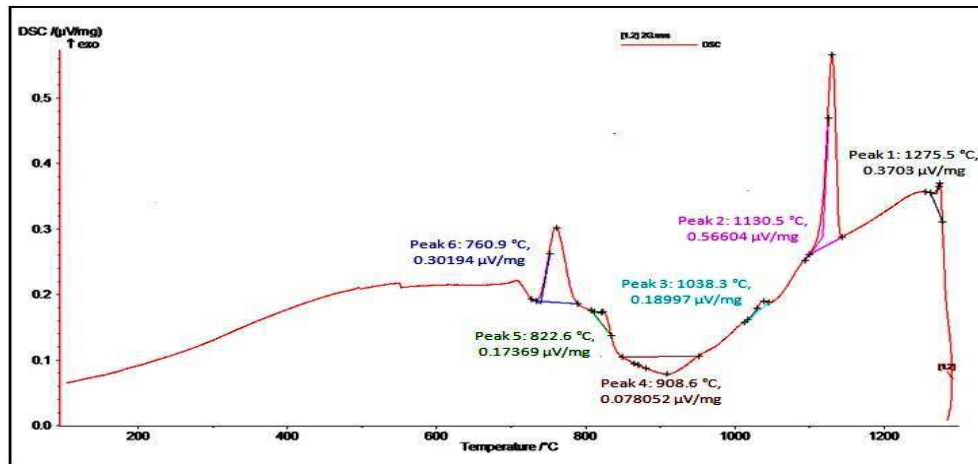


Fig 2: DSC cooling curve of 3mm- green sand SiMo

Comparing data obtained from the Thermo-Calc phase diagram shown in fig (1,a) with the DSC peaks, the solidification and solid-state phase transformations of the alloy could be summarized in table 1.

Table 1: Transformation temperatures revealed from the Thermo-Calc phase diagram vs those predicted from the peaks of the DSC

Transf.	Approx. Temp. revealed from the phase diagram	Corresponding peaks in DSC curve	Solidification and solid-state reactions during cooling
1	1200	1275.0	Liquidus: $L \rightarrow L + \gamma$
2	1170	1130.5	Eutectic reaction: $L \rightarrow \gamma + Gr + M_6C$
3	960	1038.3	Eutectoid reaction (start): $\gamma + Gr + M_6C \rightarrow \gamma + \alpha + Gr + M_6C$
4	900	908.6	Eutectoid reaction (end): $\gamma + \alpha + Gr + M_6C \rightarrow \alpha + Gr + M_6C$
5	-	822.6	Precipitation of intercellular components: $\alpha + Gr + M_6C \rightarrow \alpha + Gr + M_6C + Fe_2MoC$
6	-	760.9	Curie temperature: α non magnetic $\rightarrow \alpha$ magnetic
7	200	-	Precipitation of M_7C_3 in α

It should be noticed that the phase transformations displayed by the DSC curve confirm those suggested by the Thermo-Calc calculated phase diagram. This confirmation however is more qualitative, with some deviations in the transformation temperatures, which is expected. The phase diagram is based on equilibrium conditions, whereas DSC curve is generated at cooling rates of 30°C/min.

Microstructure of SiMo with Different Section Thickness

Specimens Cast in Greensand Molds

Fig 3 shows the microstructure of SiMo ductile iron cast in greensand mold with thickness 3, 6 and 9mm. The microstructures generally consist of spheroidal graphite with varying amounts of cell-boundary precipitates in a ferritic matrix. At small magnification of this figure, the intercellular precipitates are similar to pearlite, and its formation at the cell boundary zones in increasing

amounts with decreasing the solidification rate (or increasing the section thickness) is an indication of segregation related phenomena.

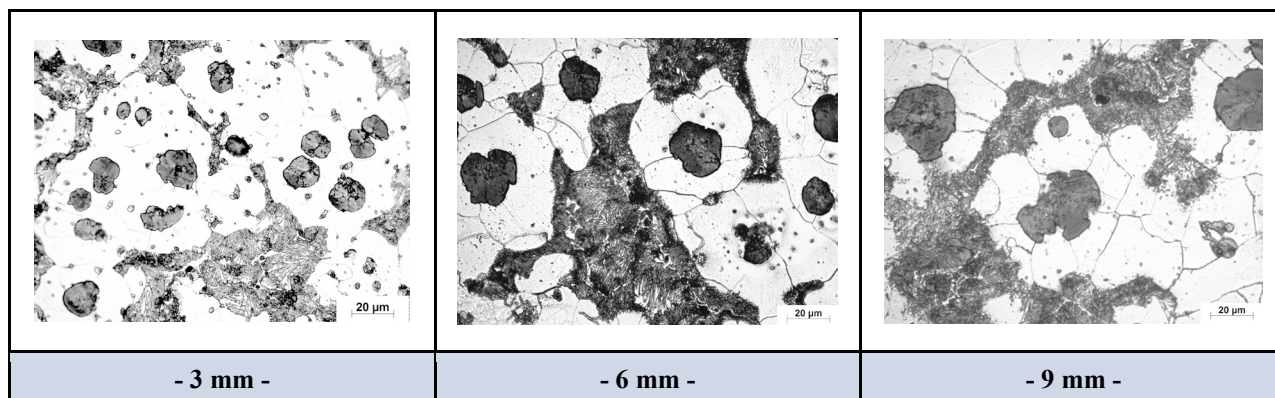


Fig 3: Microstructures of SiMo casting of 3, 6 and 9mm cast in greensand molds

Nature of Eutectic Carbides

From the phase diagram calculated using the Thermo-Calc software, the eutectic carbides are suggested to be of M_6C -type. The micrographs shown in fig 4, show that those carbides are of relatively coarse sizes with Chinese Script morphology. It may be noticed, that the Mo-content in the eutectic particles covers a wide range from 3.60 – 42.70% with varying levels of Si, which suggests that those particles may cover a wide spectrum of (Fe, Mo, Si) carbides of the M_6C -type.

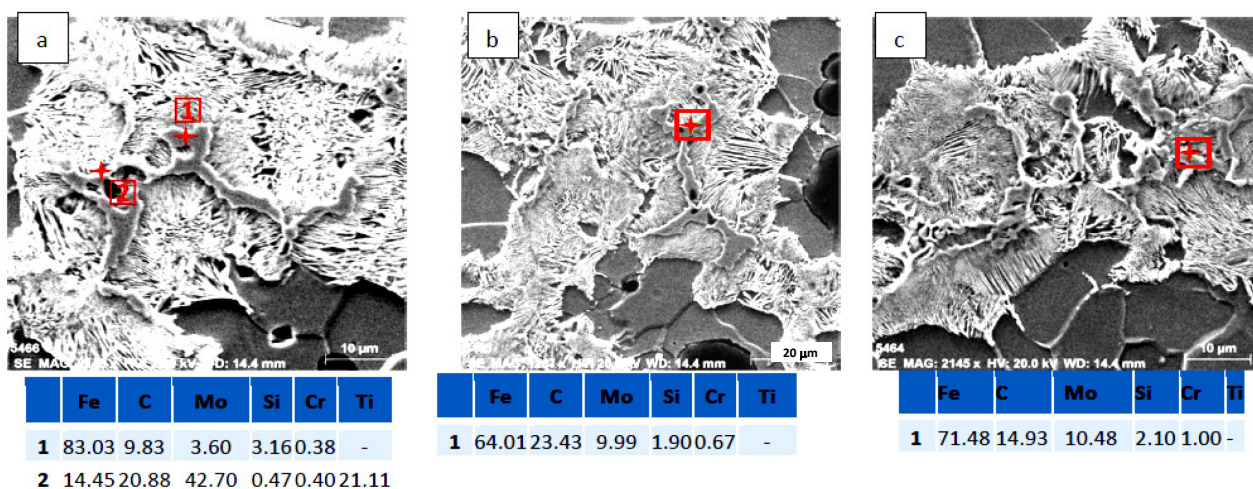


Fig 4: Composition of different eutectic carbides in SiMo 3-mm castings

Nature of Fine Precipitates

The cell-boundary components generally contain eutectic carbides embedded in the pearlite-like precipitate. Upon cooling to below eutectoid temperature, the fine precipitate, surrounding the eutectic carbides starts to form. The formation mechanism of these precipitates is still debatable. It may form due to:

- i- Austenite decomposition upon cooling as one of the eutectoid transformation products.
- ii- Pearlite decomposition subsequent to the pearlite reaction.

As indicated from Fig 1&2 and table 1, the eutectoid reaction is followed by a peak on the DSC diagram at around 822 °C, almost 86 °C after the completion of the eutectoid reaction. Such peak is most probably related to the decomposition of pearlite $\rightarrow (\alpha + M_6C)$ subsequent to the eutectoid reaction.

Fig 5 shows that in the rapidly cooled alloy (3-mm section) the lamellar structure typical of pearlite seem to be in contact with the eutectic carbide phase, which may suggest nucleation of the precipitate phase on eutectic carbides.

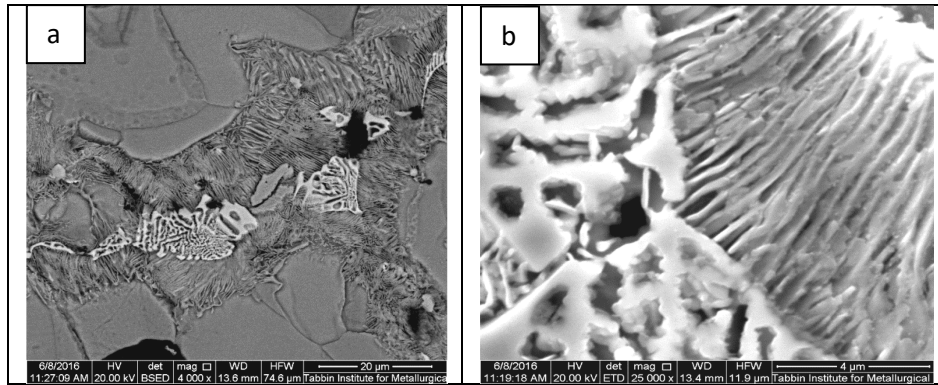


Fig 5: Nucleation of intercellular precipitates on eutectic carbides at low- and high-magnifications

For more accurate identification of the precipitate phase, both its composition and crystal lattice were determined [2], through analysis of particles in extraction replica applying selected area diffraction patterns (SADP) and convergent beam diffraction patterns (CBEP) using transmission electron microscopy. The results indicate a duplex-phase precipitate containing both Fe_2MoC and M_6C types were identified). The average analysis of the precipitate phase was found to be as follows: Fe: 68.7%, Mo: 19.0%, Si: 10.2% and Mn: 2.2%.

In the present work, the rather fine structure of the precipitate made the compositional discrimination difficult due to the resolution limits. The sequence of precipitation of the two phases is still not clear and more investigations have to be carried out to understand whether the two carbide phases precipitate concurrently or sequentially, or one or both through decomposition of pearlite or whether one forms via the decomposition of the other.

Nature of Fine Dispersed Precipitates

With decreasing the cooling rate (9-mm sections - greensand), the pearlite noticed with the higher cooling rates (3-mm sections) partially decomposes to very fine precipitate (fig 6–a). Moreover, dispersed fine precipitates were noticed in the ferrite grains (fig 6– b). These dispersed precipitates may be related to the decrease in C and Mo – solubility in ferrite. The phase diagram shown in fig 1 suggests that those fine dispersed precipitates are of the M_7C_3 type of carbides that form around 200°C during cooling as indicated in the phase diagram. EDS analysis of those precipitates revealed that they contain low Mo-contents from 3.5-6.2%, C-content from 11.2-13.0%, Si-content from 2.1-2.8% and Mn-content from 2.0-2.3%.

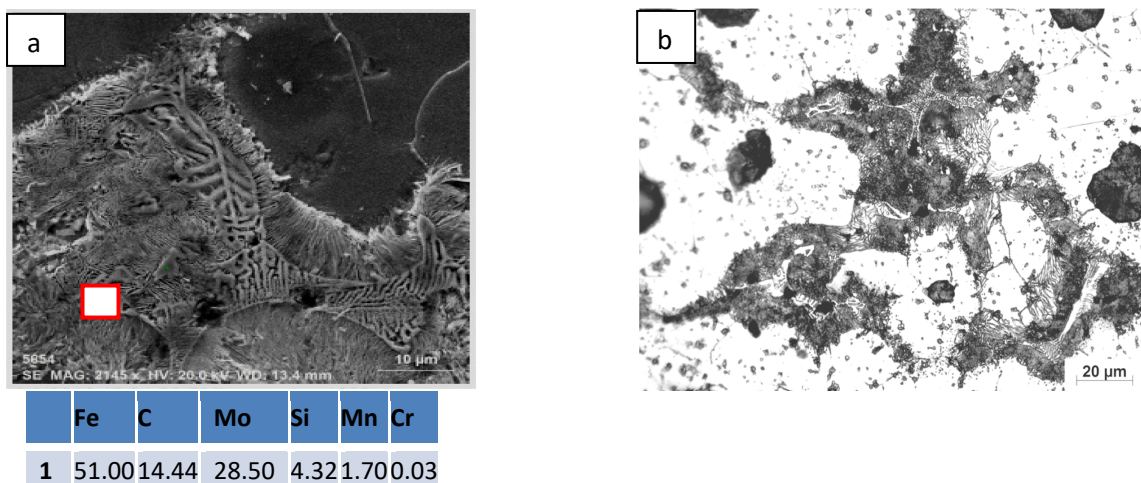


Fig 6: Microstructure of 9-mm thick plate cast in green sand mold

Specimens Cast in Investment Molds

Nature of Eutectic Carbides

The eutectic carbides formed in the rather slow cooled sections seem to be quite different in both composition and morphology. The slow solidification rates (9-mm thickness - investment mold) result in higher levels of segregation of Mo in the near vicinity of the intercellular zones. As a result, the eutectic carbides formed in those sections seem to be higher in Mo-content. The morphology of the eutectic carbides may assume blocky or fish-bone morphologies as indicated in fig (7 a, b) respectively. In both cases, the Mo-content in the eutectic carbides was over 45%.

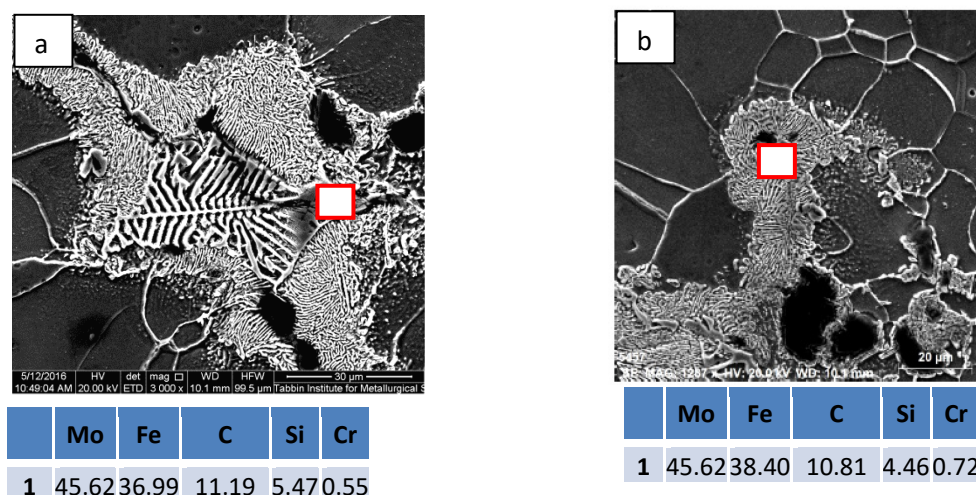


Fig 7: Intercellular eutectic and fine precipitates in the slowly cooled 9-mm thick investment mold plates

Nature of Fine Precipitates

Fig 8-a shows that the eutectic carbides formed in the highly Mo-segregated intercellular zones in the slowly cooled sections naturally contain higher contents (~48%) of Mo, whereas the rod-like precipitates formed in the very near vicinity contain much lower contents of about 2.15-2.57% Mo.

As in rapid cooling castings, the mixture of $\text{Fe}_2\text{MoC}/\text{M}_6\text{C}$ type carbides precipitates in the ferritic matrix at the intercellular regions (fig 8-b). As there are no grain boundaries between the precipitates and the ferrite grains, it is believed that the fine carbides precipitate within the ferrite after the proeutectoid and eutectoid reactions have occurred rather than form as a eutectoid transformation product. Most probably, the precipitate is formed through decomposition of the pearlite cementite surrounding the ferritic grains.

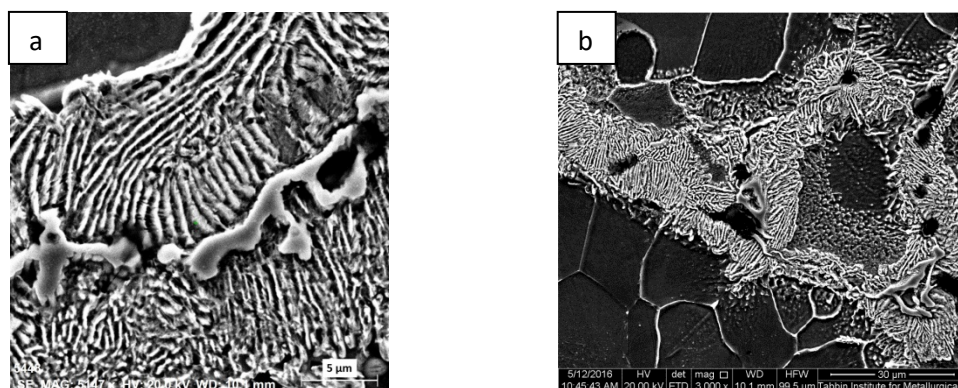


Fig 8: (a) Lower Mo-contents in the rod-like precipitate as compared to the eutectic carbides, (b) fine carbides precipitation within the ferrite grains

Chunky Graphite

It is noteworthy to mention that, in some 9-mm thick sections cast in investment cast molds, chunky graphite was encountered in the intercellular regions. Chunky graphite is generally formed in slowly cooled castings, where solidification conditions promote the segregation of rare earth elements at the grain boundaries. This segregation is as well, enhanced by poor inoculation levels [7]. In our case, the precipitation of chunky graphite, concurrently with both blocky (fig 9- a) as well as fish bone (fig 9 –b) eutectic carbides may be related to the higher Si-content in SiMo irons, higher accumulated levels of rare elements (RE) such as cerium added to the metallic charge as a component of the spheroidizing and inoculating addition, together with the slow solidification rates, which promote the segregation of RE to the intercellular regions.

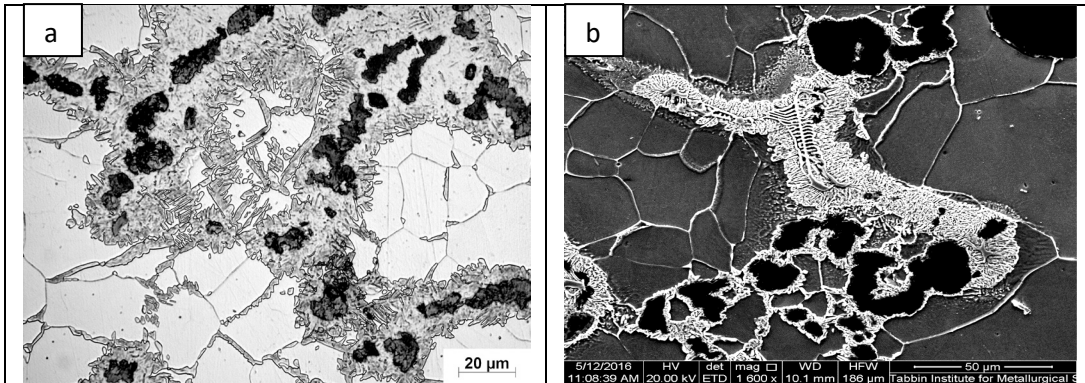


Fig 9: Formation of chunky graphite embedded in the intercellular regions.

Comparison of Fine Precipitates in Different Cooling Rates

Higher magnifications of the SEM reveal that the morphology of such precipitates is dependent on the solidification rate.

At higher cooling rates in castings of 3-mm thickness cast in greensand molds, the precipitate has lamellar structure typical of pearlite (fig 10- a), while at slower cooling rates in 9-mm thick investment cast sections, the precipitate has a rod-like shape (fig 10- b). In an earlier work [2], it has been assumed that the austenite transformation path starts with pearlite formation, and then subsequently followed by the decomposition of pearlite to the precipitate components with longer solidification time, associated with increasing section size.

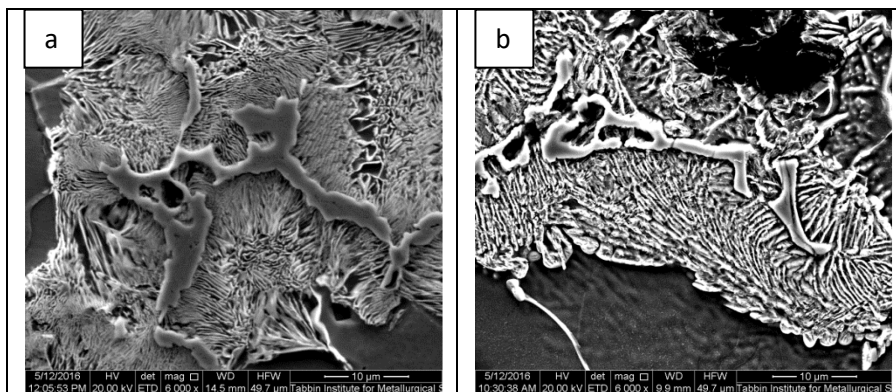


Fig 10: SEM of SiMo under different cooling rates (a) high cooling rate, 3-mm thick plates in greensand, (b) slow cooling rate, 9-mm thick plates in investment molds

Conclusions

- 1- The phase diagram of SiMo ductile irons containing 5% Si and 0.7% Mo was calculated from the Thermo-Calc software. Moreover, DSC cooling diagrams were studied. The data extracted from both diagrams were used to propose the solidification and solid-state phase transformation sequence.

- 2- Two types of carbides have been detected in the microstructure of SiMo-irons. Eutectic carbides of M_6C type were found embedded in a fine precipitate of Fe_2MoC/M_6C – type carbides in the vicinity of the intercellular regions.
- 3- Analysis of DSC data revealed that the fine precipitate forms on cooling after the completion of proeutectoid and eutectoid reactions. It is suggested that the fine precipitate forms in ferrite as a consequence of pearlitic carbides decomposition.
- 4- The morphology and composition of the eutectic carbides vary with the cooling rate. At high cooling rates the eutectic carbides have the Chinese script morphology with wide spectrum of Mo-contents. With slower cooling rates, fish-bone structures are frequently encountered with higher Mo-contents, related to higher degrees of segregations associated with slow cooling.
- 5- The morphology and composition of the fine precipitate depend on the cooling rate of the casting. At rapid cooling, the precipitate has a lamellar structure, typical of pearlite, whereas at slower cooling rate, the precipitate has a spheroidal or rod-like structure.

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