



# SOLIDIFICATION SEQUENCE AND CARBIDE PRECIPITATION IN HIGH SILICON MOLYBDENUM DUCTILE IRON (SIMO)

By

#### Mervat Youssef Abd El-Hamid Ahmed

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Metallurgical Engineering

# SOLIDIFICATION SEQUENCE AND CARBIDE PRECIPITATION IN HIGH SILICON MOLYBDENUM DUCTILE IRON (SIMO)

By

#### Mervat Youssef Abd El-Hamid Ahmed

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE

in **Metallurgical Engineering** 

Under the Supervision of

#### Prof. Dr. Abdel-Hamid Ahmed Hussein

Prof. Dr. Adel Abdel Moneim Saleh Nofal

Professor of Metallurgy
Mining, Petroleum, and Metallurgical
Department
Faculty of Engineering, Cairo University

Professor of Metal Casting Foundry Technology Laboratory Central Metallurgical for R&D Institute (CMRDI)

#### Prof. Dr. Elsayed Mahmoud Elbanna

Professor of Metallurgy Mining, Petroleum, and Metallurgical Department Faculty of Engineering, Cairo University

# SOLIDIFICATION SEQUENCE AND CARBIDE PRECIPITATION IN HIGH SILICON MOLYBDENUM DUCTILE IRON (SIMO)

By

#### Mervat Youssef Abd El-Hamid Ahmed

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

ir

**Metallurgical Engineering** 

Approved by the

**Examining Committee:** 

**Prof. Dr: Abdel-Hamid Ahmed Hussien**, Thesis Main Advisor

Prof. Dr.: Adel Abdel-Moniem Saleh Nofal, Advisor

Central Metallurgical R&D Institute (CMRDI)

**Prof. Dr: Elsayed Mahmoud Elbanna**, Advisor

**Prof. Dr: Mohammed Mamdouh Ibrahim**, Internal Examiner

**Prof. Dr.: Mohamed Abdel Wahab Waly**, External Examiner

Central Metallurgical R&D Institute (CMRDI)

Engineer's Name: Mervat Youssef Abd El-Hamid Ahmed

**Date of Birth:** 29 / 7 / 1992 **Nationality:** Egyptian

E-mail: usf.mervat@gmail.com

**Phone:** 01000632852

**Address:** 10 Mohamed kamel, Awlad Ouf,

El Haram, Giza

**Registration Date:** 1 / 10 / 2014 **Awarding Date:** / / 2018

**Degree:** Master of Science

**Department:** Mining, Petroleum and Metallurgy Engineering

**Supervisors:** 

Prof. Dr. Abdel-Hamid Ahmed Hussien, (Thesis Main Advisor) Prof. Dr. Adel Abdel Moniem Saleh Nofal, (Advisor)

Central Metallurgical R&D Institute (CMRDI)

Prof. Dr. Elsayed Mahmoud Elbanna, (Advisor)

**Examiners:** 

Prof. Dr.: Mohamed Abdel Wahab Waly, (External Examiner)

Central Metallurgical R&D Institute (CMRDI)

Prof. Dr. Mohammed Mamdouh Ibrahim, (Internal Examiner) Prof. Dr. Abdel-Hamid Ahmed Hussien, (Thesis Main Advisor) Prof. Dr. Adel Abdel Moniem Saleh Nofal, (Advisor)

Central Metallurgical R&D Institute (CMRDI)

Prof. Dr. Elsayed Mahmoud Elbanna, (Advisor)

#### **Title of Thesis:**

## SOLIDIFICATION SEQUENCE AND CARBIDE PRECIPITATION IN HIGH SILICON MOLYBDENUM DUCTILE IRON (SIMO)

#### **Key Words:**

SiMo; Thin-wall; carbides; solidification sequence; Thermal stability.

#### **Summary:**

When SiMo was introduced to be used for automotive applications, there were limitations regarding increasing service temperature.

The first point of this research aims at producing SiMo alloys and studies the effect of alloying element, inoculation type as well as influence of cooling rate on microstructure. The second point designed to study the phase transformation during solidification at different conditions. Finally, point three designed to measure the stability of the phases and determine the thermal expansion coefficient and  $A_1$  temperature.



## **Disclaimer**

I hereby declare that this thesis is my own original work and that no part of it has been submitted for a degree qualification at any other university or institute.

I further declare that I have appropriately acknowledged all sources used and have cited them in the reference section.

Name: Mervat Youssef Abd El-hamid Ahmed Date: 8/10/2018.

Signature:

### Acknowledgments

I would like to express my deep regards and sincere gratitude to Prof. Dr. Abdel-Hamid A. Hussein, Faculty of Engineering, Cairo University for his care, kind supervision, encouragement, constant efforts, and valuable stimulating guidance and fruitful discussion throughout this study.

I offer my profuse thanks with humble reverence to Prof. Adel Nofal, Foundry Technology Laboratory, Central Metallurgical Research and Development Institute (CMRDI), for his invaluable guidance and support. He was a beacon light, whose constant efforts and encouragement proved to be a parallel stimulus in completing this research successfully.

I would like to thank Prof. Dr. El-Sayed M. El-Banna, Faculty of Engineering, Cairo University for his supervision and support.

I am grateful to Prof. Dr. Mervat Ibrahim and Prof. Dr. Mohamed Morad, Foundry Technology Laboratory, Central Metallurgical Research and Development Institute (CMRDI), for their support and co-operation in the hours of need and for their expert.

Last but not least, special thanks are due to Prof. Dr Mohamed Soliman, Eng. Mostafa Othman, Eng. Mohamed Hafez, Eng. Abdel Rahman Abdel Motagaly, and the staff of Foundry Technology Laboratory of CMRDI and particularly metallographic, melting, workshop staff for their sincere help.

This work is fully supported by The Science and Technology Department Fund (STDF) under the frame work of the Korean project titled "Thin-Wall Iron Castings for Automotive Applications".

## **Table of Contents**

DISCLAIMER	I
ACKNOWLEDGMENTS	II
TABLE OF CONTENTS	III
LIST OF TABLES	V
LIST OF FIGURES	VI
NOMENCLATURE	
ABSTRACT	
CHAPTER 1 : INTRODUCTION	
CHAPTER 2 : LITERATURE REVIEW	
2.1. INTRODUCTION	
2.2. CHALLENGES AND CHARACTERISTIC PROPERTIES REQUI	
2.3. HIGH TEMPERATURE RESISTANT ALLOYS	
2.4. METALLURGY OF THIN-WALL DUCTILE IRON (TWDI)	
2.4.1. SOLIDIFICATION STAGES OF TWDI	5
2.5. THIN-WALL SILICON MOLYBDENUM DUCTILE IRON (TW-2.5.1. CHARACTERISTIC PROPERTIES OF SIMO	
2.5.1. CHARACTERISTIC PROPERTIES OF SIMO	
2.5.2. SIMO GRADES AND STANDARD SPECIFICATIONS	
2.5.3.1. EFFECT OF ALLOYING ELEMENTS	
2.5.3.2. EFFECT OF COOLING RATE	
2.5.4. MICROSTRUCTURE CONSTITUENTS OF SIMO ALLOY	
2.5.5. HEAT TREATMENT AND THERMAL STABILITY OF SIMO	
2.5.6. COEFFICIENT OF THERMAL EXPANSION	12
2.5.7. MECHANICAL PROPERTIES	13
CHAPTER 3 : EXPERIMENTAL WORK	15
3.1. RESEARCH OBJECTIVES	15
3.2. PREPARATION OF CASTINGS AND ALLOYING	15
3.2.1. MELTING	15
3.2.2. MOLD MAKING	16
3.2.3. PATTERN DESIGN	16
3.3. CHARACTERIZATION OF SIMO	17
3.3.1. CHEMICAL COMPOSITION ANALYSIS	17
3.3.2. SOLIDIFICATION STUDIES	17
2.5.3.1. THERMO-CALC CALCULATIONS	17
2.5.3.2. DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS	
3.3.3. METALLOGRAPHIC ANALYSIS	
3.3.4. THERMAL STABILITY EXPERIMENTS	18
CHAPTER 4: RESULTS AND DISCUSSION	19
4.1. CHARACTERIZATION OF SIMO	19
4.1.1. CHEMICAL COMPOSITION ANALYSIS	19
4.1.2. SOLIDIFICATION STUDIES	19
4 1 2 1 THERMO-CALC CALCUL ATIONS	10

4.1.2.2.	DIFFERENTIA	L SCANNING CALORIME	TRY (DSC) ANALYSIS	23
4.1.3. ME	ETALLOGR <i>A</i>	APHIC ANALYSIS		32
			ULANT TYPE AND ALLO	
4.1.3.2.			OF THE DEVELOPED SIN	
4.2. HEAT	TREATM	ENT	•••••	60
			MENSIONAL STA	
			•••••	

## **List of Tables**

Table 2.1: Chemical composition of SiMo ductile cast irons, given in wt% (Fe bal.)6
Table 3.1: The chemical composition of the three inoculants used17
Table 3.2: The planned chemical composition of TW-Si-Mo plates17
Table 4.1: The final chemical composition of of TW-Si-Mo plates19
Table 4.2: The effect of inoculant type and alloying elements on the amount percent of
the phases in room temperature and transformation temperatures22
Table 4.3: Comparison between the amount of phases in alloyed and alloyed SiMo23
Table 4.4: SiMo ductile iron transformation peaks in cooling and heating27
Table 4.5: Alloyed SiMo ductile iron transformation peaks in cooling and heating30
Table 4.6: Transformation temperatures revealed from the Thermo-Calc phase diagram
vs those predicted from the peaks of the DSC in SiMo31
Table 4.7: Transformation temperatures revealed from the Thermo-Calc phase diagram
vs those predicted from the peaks of the DSC in alloyed SiMo31
Table 4.8: Microstructure calculations (EN ISO 945-1): Spherodial Number, Shape and
Size Index of Graphite for unetched samples32

## **List of Figures**

Figure 2.1: 3D model of exhaust system of 6-cylinder diesel engine2
Figure 2.2: Properties required for high efficient exhaust system parts
Figure 2.3: The relationship between exhaust materials selection and operation
conditions3
Figure 2.4: Typical microstructure of SG iron4
Figure 2.5: Simulated undercooling below the extrapolated lines for austenite5
Figure 2.6: Modelling with including and excluding the possibility of austenite
dendrites nucleation5
Figure 2.7: Effect of silicon content on: (a) the critical temperature, (b) oxidation in air
at 650°C (c) room temperature mechanical properties of ferritic Ductile Iron
Figure 2.8: Chemistry map for high-Si SiMo as related to regarding C, Si, and CE.
Prediction of microstructure and shrinkage is also plotted8
Figure 2.9: Casting experiments and modeling of shrinkage for high-Si SiMo of 4.5%
Si. The C content is $3.35\%$ , i.e. $CE = 4.85$ for the top row of pictures, while the C
content is 3.15%, i.e. CE = 4.65 for the bottom pictures. The pictures in the left, middle,
and right columns represent the flange sections of manifolds, sections of AFS blind
risers, and solidification modeling respectively.
Figure 2.10: Etched (Nital 2%) microstructure of SiMo, showing graphite nodules
dispersed in ferrite (white) with carbides of M <sub>6</sub> C-type (M=Fe, Mo, Si), formed in the
intercellular regions
Figure 2.11: Micrograph images showing the etched (Nital 2%) microstructure of
SiMo with additions of a) none, b) 0.5wt% Cr, c) 1wt% Cr, d) 0.3wt% Cr, 1wt% Ni, e)
0.6wt% Cr, 1wt% Ni and f) 1wt% Ni. Scale bars indicate 200μm
Figure 2.12: Phase diagrams calculated by Thermo-Calc for SiMo with additions of a)
Cr , b) Ni11
Figure 2.13: Intercellular region of SiMoshowing a) micrograph image of M <sub>6</sub> C
carbides and spheroidized pearlite in a ferritic matrix and b) SEM image of an M <sub>6</sub> C
carbide
Figure 2.14: Intercellular region of SiMowith additions of 0.6Cr and 1Ni showing a)
micrograph image of M <sub>6</sub> C and Cr-rich carbides and spheroidized pearlite in a ferritic
matrix and b) SEM image of a mixed carbide of M <sub>6</sub> C and a Cr-rich phase11
Figure 2.15: Coefficient of thermal expansion alpha versus temperature measured from
dilatometer testing at a heating rate of 5 o C/min: (a) SiMo of 4% Si and (b) high-Si
SiMo of 4.9% Si. The critical temperature A1 can be determined from the curves12
Figure 2.16: Silicon content versus room temperature properties: (a) tensile UTS and
0.2% offset YS, (b) tensile elongation E%, and (c) Brinell hardness HBW. Mo content
varied from 0.6% to 0.9%. Each point represents three tests at least
Figure 2.17: Silicon content versus the hot tensile UTS tested at different temperatures.
Each point represents the average of three tests at least. The points are connected just
for showing the tendency to change. Mo content is 0.75%
Figure 2.18: Room temperature tensile results of as-cast, subcritically annealed, and full
annealed specimens of high-Si SiMo (4.65% Si and 0.75% Mo)
Figure 2.19: Absorbed energy of non-notched Charpy testing for 4.65% Si and 5.01%
Si SiMo samples with different treatment: as-cast, subcritical annealing, and full
annealing respectively. The sample dimension is $10\times10\times55$ mm14

Figure 3.1: a) A typical vortex unit is made up for major cast iron and steel
components: (A) refractory, (B) additives hopper, (C) interchangeable calibrated orifice
and (D) shut off slide, b) Vortex unit available at CMRDI
Figure 3.2: Production of investment molds
Figure 3.3: The stepped pattern used for the preparation of casting molds
Figure 3.4: Quenching LINSIES L87 dilatometer available at CMRDI
Figure 4.1: Thermo-Calc phase diagram (a) SiMo (A1 at 1170°C), (b)Alloyed SiMo
1%Cr, 0.7% V, 0.6% Ni (A1 at 1160°C)
Figure 4.2: Mass percent of the components in carbides (a) M6C, (b) M7C3 where
M=Fe, Mo, Si, Mn
Figure 4.3: Volume fraction of all phases in SiMo with three different inoculants21
Figure 4.4: Volume fraction of all phases in Alloyed SiMo (1%Cr, 0.7%V, 0.6% Ni)
with three different inoculants
Figure 4.5: Cooling DSC curve of Si-Mo Ductile Iron (Green Sand – Inc. 2)
Figure 4.6: Cooling DSC curve of Alloyed Si-Mo Ductile Iron – Green Sand – Inc.2
inoculation
Figure 4.7: N.C vs thickness for unalloyed samples
Figure 4.8: N.C vs thickness for unalloyed samples
Figure 4.9: Microstructures of SiMo casting of 3, 6 and 9mm cast in greensand molds-
Inc.246
Figure 4.10: Composition of different eutectic carbides in SiMo 3mm castings, Inc.2.47
Figure 4.11: Nucleation of intercellular precipitates on eutectic carbides at low- and
high-magnifications
Figure 4.12: Microstructure of 9-mm thick plate cast in green sand mold48
Figure 4.13: Intercellular eutectic and fine precipitates in the slowly cooled 9-mm thick
investment mold plates49
Figure 4.14: (a) lower Mo-contents in the rod-like precipitate as compared to the
eutectic carbides, (b) fine carbides precipitation within the ferrite grains49
Figure 4.15: Formation of chunky graphite embedded in the intercellular regions 50
Figure 4.16: 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
50
Figure 4.17: The optical microstructure of alloyed SiMo samples a) 3mm, b) 6mm and
c) 9mm
Figure 4.18: Optical micrograph, SEM, and EDS analysis for SiMO-Cr-Ni-V, Green
Sand, 3mm, Inc. 1(4G-3mm)
Figure 4.19: Optical and SEM Microstructure for SiMO-Cr-Ni-V, Green Sand, 3mm,
Inc. 2 (5G-3)
Figure 4.20: Optical and SEM Microstructure for SiMO-Cr-Ni-V, Investment Mold,
3mm, Inc. 1 (4I-3mm)
Figure 4.21: Optical and SEM Microstructure for SiMO-Cr-Ni-V, Investment Mold,
9mm, Inc. 1 (4I-9mm)
Figure 4.22: Optical and SEM Microstructure for SiMO-Cr-Ni-V, Investment Mold,
9mm, Inc.2 (5I-9mm)
Figure 4.23: Optical microstructure of high-silicon molybdenum ductile iron, 3mm
/Unalloyed /green Sand, (A) As-cast (B) Annealing 1080°C (C) Normalizing 1080°C.61
Figure 4.24: Optical microstructure of high-silicon molybdenum ductile iron, 9mm
/Unalloyed /Investment, (A) As-cast (B) Annealing 1080°C (C) Normalizing 1080°C.61
Figure 4.25: Change in length vs temperature of unalloyed and alloyed SiMo irons of 3
mm thickness
11111 UIICKIICSS

Figure 4.26: Change in length vs time of unalloyed and alloyed SiMo irons64
Figure 4.27: Optical microstructure of high-silicon molybdenum ductile iron, As cast
/Unalloyed /Greensand, (A) 3mm (B) 6mm (C) 9mm65
Figure 4.28: Optical microstructure of high-silicon molybdenum ductile iron, As Cast
/Unalloyed /Investment, (A) 3mm (B) 6mm (C) 9mm65
Figure 4.29: Optical microstructure of high-silicon molybdenum ductile iron, After
Dilatometer/Unalloyed / Greensand, (A) 3mm (B) 6mm (C) 9mm66
Figure 4.30: Optical microstructure of high-silicon molybdenum ductile iron, After
Dilatometer/Unalloyed / Investment, (A) 3mm (B) 6mm (C) 9mm66
Figure 4.31: Optical microstructure of high-silicon molybdenum ductile iron, As cast
/Alloyed /Greensand, (A) 3mm (B) 6mm (C) 9mm67
Figure 4.32: Optical microstructure of high-silicon molybdenum ductile iron, As Cast
/Alloyed /Investment, (A) 3mm (B) 6mm (C) 9mm67
Figure 4.33: Optical microstructure of high-silicon molybdenum ductile iron, After
Dilatometer /Alloyed /Greensand, (A) 3mm (B) 6mm (C) 9mm68
Figure 4.34: Optical microstructure of high-silicon molybdenum ductile iron, After
Dilatometer / Alloyed / Investment, (A) 3mm (B) 6mm (C) 9mm68

### **Nomenclature**

SEM Scanning Electron Microscopy

OM Optical Metallography

EDS Energy Dispersive X-Ray Spectroscopy
DSC Differential Scanning Calorimetry
CTE Coefficient of Thermal Expansion

SG Spheroidal Graphite

TW Thin-Wall

TWDI Thin-Wall Ductile Iron

A<sub>1</sub> Austenite to ferrite transformation temperature.

FCC Face Center Cubic BCC Body Center Cubic

BHN Brinell Hardness Number

GS Green Sand INV Investment Mold

Inc Inoculation

#### **Abstract**

The automotive industry is concerned with fuel economy and gas emissions; whereas the cost consideration is customer mandated. Silicon Molybdenum ductile Iron (SiMo) is characterized with its combination of low cost and unique properties in high temperature applications, such as automotive parts like exhaust manifolds and turbocharger housings, furnace applications and turbine castings. A typical chemical composition of SiMo ductile iron contains 4% Si and 0.5-2.0% Mo and can be used up to 840-850°C.

The main objective of this research aims at developing technology to produce high quality thin wall castings and to introduce new grades of SiMo castings with specific properties that add to the performance of ductile iron castings in special high temperature applications. This research also aimed at reaching a better understanding of the influence of the cooling rate, inoculants chemistry and alloying elements such as Cr, Ni and V on the formation of precipitates in SiMo ductile irons.

In order to achieve these objectives, different molds of 3, 6, 9 mm thickness were prepared from greensand and ceramic material to give different cooling rates.

Optical metallography (OM) as well as Scanning Electron Microscopy (SEM) were used to clearly show the different phases, i.e., eutectic carbides and fine precipitates. Moreover, Energy Dispersive X-Ray Spectroscopy (EDS) analysis was followed to reach a semi - quantitative estimate of the relevant compositions. The solidification sequence as well as solid-state transformations were followed using phase diagram calculation via Thermo-Calc software, Differential Scanning Calorimetry (DSC) and dilatometry analysis.

Intensive SEM and EDS investigations have detected three types of carbides 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. It is showed that the eutectic carbides are mainly (Fe, Mo, Si) Carbides containing up to 48% Mo, whereas the fine precipitate carbides contain lower Mocontents. Both carbide types did not appear to have a strict stoichometric composition. The third type of carbides is fine dispersed precipitate of  $M_7C_3$  in ferrite.

In alloyed SiMo angular carbides and dot-like carbide were clearly observed in the microstructure of the alloyed SiMo samples. The eutectic carbides are mainly (Fe, Mo, Cr, V, Ni) carbides with Mo-content reaching 45%, whereas the fine precipitate is of more complex nature with lower Mo-contents.

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.

DSC data revealed that the fine precipitate forms on cooling below the lower critical temperature after the completion of proeutectoid and eutectoid reactions.

The dilatometer charts showed similar expansion behavior for both investment and green sand molds of the three different thicknesses at elevated temperature. The maximum operation temperature of the unalloyed SiMo alloys is 900 °C which is high enough when compared to the other tradition SiMo alloys in the market (max operation temperature 700-750 °C). In alloyed SiMo samples with the same thickness (Green sand and investment) showed a decrease in the  $A_1$  temperature by about 30 to 50 °C. This apparently because of the 0.6% Ni which plays as austenite stabilizer.

### **Chapter 1: Introduction**

Silicon Molybdenum Ductile Iron (SiMo) is a special purpose heat resistant alloy which is considered to be the cheapest material compared to other austenitic alloys [1-3]. Moreover, SiMo can keep the dimensions without any changes for high numbers of cycles that can range from below freezing temperatures to very high temperatures up to 850°C. These properties nominates SiMo alloys to be suitable for automotive applications as exhaust manifolds and turbocharger housings, furnace applications and turbine castings [2]. However, When the operation temperature is increased, SiMo alloys show limitations unlike the very expensive austenitic alloys with its higher strength at high operation temperatures due to their FCC structure which has fewer slip systems making it difficult for deformations to happen and permits larger amounts of interstitial carbon in the structure compared to ferrite, which has a BCC structure, resulting in a higher solid solution strengthening effect in austenite [1][3][4].

So, the current objectives are currently being tackled through three trends: First, technological development to produce thin wall castings, down to 3 mm wall thickness. Second, development of new grades of SiMo castings, with specific properties, that adds to the performance of ductile iron castings in special high temperature applications. Third, study the solidification sequence and carbides nature and morphology.

The studied parameters include: chemical composition of the SiMo alloys with three inoculants chemistry, different cooling rate by using two molding techniques (investment casting and greensand), thermal and dimensional stability and heat treatment. The impact of these parameters on solidification behavior studied using advanced thermal analysis techniques, thermodynamic and kinetic analysis, DSC and dilatometry analysis.

The physical properties including thermal expansion, was also evaluated as related to the different metallurgical and technological conditions involved in the production process.