



PRODUCTION OF SILICOMANGANESE ALLOY FROM EGYPTIAN LOW GRADE MANGANESE ORES

By

Esraa Mahmoud Kotb Ataby

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
Chemical Engineering

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2020

PRODUCTION OF SILICOMANGANESE ALLOY FROM EGYPTIAN LOW GRADE MANGANESE ORES

By
Esraa Mahmoud Kotb Ataby

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
Chemical Engineering

Under the Supervision of

Prof. Dr. Magdi Fouad Abadir

Professor of Inorganic Industries
Chemical Engineering Department
Faculty of Engineering, Cairo University

**Prof. Dr. Hoda Salama Rabie El-
Faramawy**

Professor in Steel and Ferroalloys Lab.,
Head of Metals Division
Central Metallurgical Research and
Development Institution (CMRDI)

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2020

PRODUCTION OF SILICOMANGANESE ALLOY FROM EGYPTIAN LOW GRADE MANGANESE ORES

By
Esraa Mahmoud Kotb Ataby

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
Chemical Engineering

Approved by the
Examining Committee

Prof. Dr. Magdi Fouad Abadir, Thesis Main Advisor

Prof. Dr. Hafez Abdel-Azim Ahmed, Internal Examiner

Prof. Dr. Mahmoud Ibrahim Abbas El-Sonbaty, External Examiner

- Emeritus professor at Material Science Engineering
Department, Suez University

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2020

Engineer's Name: Esraa Mahmoud Kotb Ataby
Date of Birth: 7/12/1992
Nationality: Egyptian
E-mail: esraamahmoud71292@gmail.com
Phone: (+2) 01157625376
Address: 15 May City, Helwan, Cairo
Registration Date: 1/3/2016
Awarding Date:/....../2020
Degree: Master of Science
Department: Chemical Engineering



Supervisors:

Prof. Magdi Fouad Abadir
Prof. Hoda Salama Rabiea El-Faramawy

Examiners:

Prof. Mahmoud Ibrahim Abbas (External examiner)
Emeritus professor at Material Science
Engineering Department, Suez University
Prof. Hafez Abdel-Azim Ahmed (Internal examiner)
Prof. Magdi Fouad Abadir (Thesis advisor)

Title of Thesis:

Production of Silicomanganese Alloy from Egyptian Low grade Manganese Ores

Key Words:

Low grade manganese ore Carbo-thermic reduction process; Smelting process Pyro-metallurgical process Submerged arc furnace; Low manganese pig iron; Manganese rich slag; Silicomanganese

Summary:

In the last years, it has become a great necessary to develop a new technology for utilizing the unused huge amounts of low grade manganese ores with Mn/Fe ratio equals 0.6-1 in the production of silicomanganese due to the gradual depletion of high grade manganese ores reserves. This target can be achieved through a double smelting process in submerged arc furnace. The first process is a carbo-thermic reduction of low grade manganese ore in presence of coke and quartzite to produce low manganese pig iron (2-3% Mn by weight) and high manganese slag with high Mn/Fe ratio reaching about 9 which is suitable after that in the production of silicomanganese. The second smelting process is a carbo-thermic reduction of the produced manganese rich slag in presence of medium grade manganese ore, quartzite, coke and dolomite for production of standard silicomanganese (Si16Mn63 and Si17Mn65). The parameters affecting on the reduction of low grade manganese ore which are power, reducing agent and charge basicity were investigated. The parameters affecting the production process of silicomanganese, namely, the reducing agent, charge basicity and Mn/Si ratio were also investigated. Finally, the optimum conditions obtained for the two processes were applied on a 0.1 MVA pilot scale submerged arc furnace.

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 references section.

Name: Esraa Mahmoud Kotb

Date: 17/2/2020

Signature:

Dedication

I would like to dedicate this work to My Parents for their patience and continuously supporting me in every hard time.

Acknowledgments

I would like to express my thanks and great appreciation to **Prof. Dr. Magdi Abadir** for his help as he did not hesitate to present any assistance in this work.

My great appreciation and gratitude lies to **Prof. Dr. Hoda El-Faramawy** who designed the work plan and was able to present solutions for the technical problems that arose through the work. I am grateful to her for all the knowledge and experience she shared with me that enabled me carrying out this work. Besides that she gave me continuous moral support and encouragement that enabled me to submit that thesis in due time. I really would like to thank her for everything she was done for me.

Special thanks are also due to **Prof. Dr. Michael Mishreky, Prof. Dr. Mamdouh Eissa, Prof. Dr. Azza Mohamed and Prof. Dr. Saeed Ghali** for their sincere help and valuable advices.

I also wish to express my deep thanks to **Sinai Manganese Company (SMC)** for supplying all the raw materials used in this work.

This study is a part of different activities performed in the frame of an applied project in a technological alliance for deepening and maximizing the local manufacturing of mineral resources in Sinai financed by the **Academy of Science and Technology** (ASRT), Egypt. I would like to acknowledge the Academy of Science and Technology due to the financial support and all facilities offered to perform this work.

Table of Contents	Page
LIST OF TABLES	vii
LIST OF FIGURES	viii
NOMENCLATURE	xi
ABSTRACT	xii
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: LITERATURE REVIEW	3
2.1 Manganese ores	3
2.1.1 Manganese ore uses	3
2.1.2 Manganese ore minerals	4
2.1.3 Manganese ore grades	5
2.2 Global production and reserves of manganese ores	5
2.3 Egyptian manganese ores	7
2.4 Current global challenge	8
2.5 Beneficiation methods of low grade manganese ores	9
2.5.1 Ore dressing methods	9
2.5.2 Hydrometallurgical methods	9
2.5.3 Pyro-metallurgical method	10
2.6 Carbo-thermic reduction process of low grade manganese ores in submerged arc furnace	10
2.6.1 Reaction mechanism of carbo-thermic reduction process of low grade manganese ores	11
2.6.2 Thermodynamic aspects of the Mn-O-C system	11
2.6.3 Factors affecting the reduction process of low grade manganese ores	13
2.6.3.1 Effect of power (Effect of process temperature)	13
2.6.3.2 Effect of coke	14
2.6.3.3 Effect of charge basicity	14
2.7 Ferroalloys	15
2.7.1 Definition and uses of ferroalloys	15
2.7.2 Classifications of ferroalloys	15
2.8 Importance of silicomanganese	16
2.9 Global production statistics of silicomanganese	17
2.10 Standards of silicomanganese	18

2.11 Raw materials	18
2.11.1 Manganese ores	19
2.11.2 High carbon ferromanganese slag (HC-FeMn slag)	19
2.11.3 Quartzite	19
2.11.4 Coke	20
2.11.5 Flux agent	20
2.12 Production processes of silicomanganese	21
2.13 Production technology of silicomanganese on submerged arc furnace	22
2.13.1 Physical zones in submerged arc furnace	24
2.13.2 Reduction mechanism of manganese ores	27
2.14 Thermodynamic considerations in silicomanganese production process	30
2.14.1 The distribution of Mn between the alloy and slag phases	30
2.14.2 The distribution of Si between the alloy and slag phases	32
2.14.3 Formation of silicon carbides	34
2.15 Carbo-thermic reduction process for production of silicomanganese from manganese rich slag produced from low grade manganese ore	35
2.15.1 Factors affecting the production of silicomanganese	36
2.15.1.1 Effect of coke	36
2.15.1.2 Effect of charge basicity	36
2.15.1.3 Effect of Mn/Si ratio	37
2.16 Aim of the study	37
CHAPTER 3: EXPERIMENTAL WORK	38
3.1 Raw materials characterizations	38
3.1.1 Mineralogical analysis	38
3.1.2 Chemical analysis	39
3.2 Preparation of the raw materials, refractories and the submerged arc furnace	40
3.3 Production of silicomanganese from Om Bogma manganese ores	40
3.3.1 Bench scale experimental heats.	40
3.3.1.1 Bench scale furnace description	41
3.3.1.2 Smelting technique	42
3.3.1.3 The casting process	43
3.3.2 Pilot scale experimental heats	44
3.3.2.1 Furnace description	44

3.3.2.2 The pilot scale production	45
3.3.2.3 Casting of the products	45
3.4 Products characterizations	46
CHAPTER 4: RESULTS AND DISCUSSIONS	48
4.1 Raw materials	48
4.1.1 Mineralogical analysis of manganese ores	48
4.1.2 Chemical analysis of raw materials	49
4.1.2.1 Manganese ores	49
4.1.2.2 Quartzite and fluxing materials	50
4.1.2.3 Coke and coke ash	51
4.2 Production of silicomanganese from Om Bogma manganese ores	51
4.3 Smelting of low grade manganese ore for production of high manganese slag and pig iron	52
4.3.1 Factors affecting the smelting process of Om Bogma low grade manganese ore	52
4.3.1.1 Effect of power	52
4.3.1.2 Effect of coke ratio	57
4.3.1.3 Effect of charge basicity	61
4.3.2 Implementing the optimum condition on 0.1 MVA pilot scale submerged arc furnace	65
4.4 Production of silicomanganese from the prepared high manganese slag from low grade manganese ore	69
4.4.1 Factors affecting the production of silicomanganese alloy	69
4.4.1.1 Effect of coke ratio	69
4.4.1.2 Effect of charge basicity	73
4.4.1.3 Effect of Mn/Si Ratio of the charge	78
4.4.2 Implementing the optimum condition on 0.1 MVA pilot scale submerged arc furnace	82
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	85
REFERENCES	87
APPENDIX A	93
APPENDIX B	96
APPENDIX C	103

List of Tables	Page
Table 2.1: Common manganese minerals in manganese ore deposits	5
Table 2.2: World mine production and reserves of manganese ores	6
Table 2.3: Classification of Om Bogma manganese ores	8
Table 2.4: Chemical composition of eastern desert manganese ore	8
Table 2.5: Other localities of manganese ore deposits	8
Table 2.6: SiMn grades according to ISO 5447-80 and GOST 4756-91	18
Table 2.7: SiMn grades according to GOST 4756-78	18
Table 2.8: SiMn specification according to ASTM A483-2010	18
Table 4.1: Chemical composition of Om Bogma low and medium grade Mn ores	49
Table 4.2: Chemical composition of quartzite	50
Table 4.3: Chemical composition of dolomite	50
Table 4.4: Chemical composition of bauxite	50
Table 4.5: Chemical composition of coke	51
Table 4.6: Chemical composition of coke ash	51
Table 4.7: Experimental heats for studying the power effect on reduction of low grade Mn ore	53
Table 4.8: Experimental heats for studying the coke ratio effect on reduction of low grade Mn ore	58
Table 4.9: Experimental heats for studying the basicity effect on reduction of low grade Mn ore	62
Table 4.10: Pilot scale experimental heats for production of Mn rich slag and pig iron	66
Table 4.11: Chemical composition of the pilot production of Mn rich slag	67
Table 4.12: Experimental heats for studying the coke ratio effect on smelting of SiMn	70
Table 4.13: Experimental heats for studying the basicity effect on smelting of SiMn	74
Table 4.14: Experimental heats for studying the Mn/Si ratio effect on smelting of SiMn	79
Table 4.15: Pilot scale experimental heats for production of SiMn alloy	83

List of Figures	Page
Figure 2.1: Annual crude steel production through 2011-2018	4
Figure 2.2: Total world production of manganese ores through 2012-2019	7
Figure 2.3: Total world production and demand of manganese ores through 2013-2019	7
Figure 2.4: Ellingham diagram for Mn–O–C system at 1 atm	12
Figure 2.5: Thermodynamic equilibrium composition for mixture of MnO ₂ and carbon as a function of carbon content at 25, 75 and 150 °C and 1 atm.	13
Figure 2.6: Total world production and demand of SiMn through 2013-2019	17
Figure 2.7: Top 10 producing SiMn countries	17
Figure 2.8: Simplified schematic diagram for SiMn production on one step	21
Figure 2.9: Simplified schematic diagram for FeMn and SiMn processes integration (Duplex process)	22
Figure 2.10: Schematic diagram of SAF and its main parts	24
Figure 2.11: Main physical zones inside SAF	27
Figure 2.12: Reduction mechanism along producing SiMn SAF	29
Figure 2.13: Complete equilibrium relations for MnO-SiO ₂ -CaO slag system in equilibrium with Mn-Si-C _{sat} alloy at P _{CO} =1atm	31
Figure 2.14: Effect of Al ₂ O ₃ addition on equilibrium MnO content in MnO-SiO ₂ -CaO-Al ₂ O ₃ slag system	32
Figure 2.15: Effect of temperature on silicon content in MnO-SiO ₂ -CaO-Al ₂ O ₃ slag systems in equilibrium with Mn-Si-C _{sat} alloy at CaO/Al ₂ O ₃ = 4	33
Figure 2.16: Silicon distribution as a function of basicity	34
Figure 2.17: The relation between Si content and carbon solubility in SiMn alloy	35
Figure 2.18: Simplified schematic diagram for production of SiMn from low grade Mn ore	35
Figure 3.1: X-Ray diffraction analysis system	39
Figure 3.2: X-Ray fluorescence analysis system	39
Figure 3.3: Bench scale submerged arc furnace	41
Figure 3.4: Smelting process on the bench scale furnace	43
Figure 3.5: Casting process of the produced metal and slag	43
Figure 3.6: 0.1 MVA pilot scale submerged arc furnace.	44
Figure 3.7: Casting process on 0.1 KVA pilot scale submerged arc furnace	45

Figure 3.8: Portable thermo scientific Niton XL3t XRF analyzer with GOLDD technology	46
Figure 3.9: Combustion Master Carbon Sulfur analyzer	46
Figure 3.10: Belec Vario Lab 2C spectro photometer	47
Figure 4.1: XRD pattern for low grade manganese ore	48
Figure 4.2: XRD pattern for medium grade manganese ore	49
Figure 4.3: Effect of power in pre-reduction stage and total power on the metallic yield of pig iron	55
Figure 4.4: Effect of power in pre-reduction stage and total power on the Fe recovery in the pig iron	55
Figure 4.5: Effect of power in pre-reduction stage and total power on the Mn recovery in the pig iron	56
Figure 4.6: Effect of power in pre-reduction stage and total power on the unreduced MnO recovery in the Mn rich slag	56
Figure 4.7: Effect of power in pre-reduction stage and total power on the unreduced FeO recovery in the Mn rich slag	57
Figure 4.8: Effect of coke ratio on metallic yield of pig iron	59
Figure 4.9: Effect of coke ratio on Mn and Fe recoveries in the pig iron	59
Figure 4.10: Effect of coke ratio on unreduced MnO and FeO recoveries in the Mn rich slag	61
Figure 4.11: Effect of charge basicity on metallic yield of pig iron	63
Figure 4.12: Effect of charge basicity on Mn and Fe recoveries of pig iron	64
Figure 4.13: Effect of charge basicity on unreduced MnO and FeO recoveries of Mn rich slag	64
Figure 4.14: Effect of quartzite amount on unreduced MnO% in Mn rich slag	65
Figure 4.15: Bench scale produced pig iron and Mn rich slag samples	67
Figure 4.16: Pilot scale produced pig iron samples	68
Figure 4.17: Pilot scale produced Mn rich slag before and after crushing	68
Figure 4.18: Effect of coke ratio on metallic yield of SiMn	71
Figure 4.19: Effect of coke ratio on Mn and Si recoveries of SiMn	71
Figure 4.20: The relation between Si and C content in SiMn alloy	73
Figure 4.21: Effect of basicity on metallic yield of SiMn	75
Figure 4.22: Effect of basicity on Mn and Si recoveries of SiMn	75
Figure 4.23: Effect of discard slag basicity on the slag viscosity	78
Figure 4.24: Metal particles entrapped in the discard slag	78
Figure 4.25: Effect of Mn/Si ratio on metallic yield of SiMn	80
Figure 4.26: Effect of Mn/Si ratio on Mn and Si recoveries of SiMn	80

Figure 4.27: Effect of Mn/Si ratio on Mn and Si (%wt.) in SiMn	82
Figure 4.28: Bench scale produced SiMn samples	84
Figure 4.29: Pilot scale produced SiMn samples	84

Nomenclature

Submerged Arc Furnace

Silicomanganese

High Carbon Ferromanganese Slag

Mega Ton

Mega Volt Ampere

International Organization for Standardization

State Standard of the Soviet Union

American Society for Testing and Materials

SAF

SiMn

HC-FeMn slag

MT

MVA

ISO

GOST

ASTM