

CERTIFICATE

It is certified that the work contained in the thesis titled '**High temperature oxidation, metal dusting, erosion and corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel**' by **Sharvan Kumar** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of comprehensive examination, Candidacy, and SOTA for the award of Ph. D. degree.

Supervisor

Dr. G.S. Mahobia
(Associate Professor)
Department of Metallurgical Engineering
Indian Institute of Technology (BHU), Varanasi

DECLARATION BY THE CANDIDATE

I, *Sharvan Kumar*, certify that the work embodied in this thesis is my bonafide work and carried out by me, under the supervision of *Dr. G.S. Mahobia* from *July 2017 to March 2022* at the '*Department of Metallurgical Engineering*', Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my work.

Date:

Place: Indian Institute of Technology (BHU), Varanasi

(Sharvan Kumar)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Supervisor

Dr. G.S. Mahobia (Associate Professor)
Department of Metallurgical Engineering
Indian Institute of Technology (BHU), Varanasi

Professor and Head

Department of Metallurgical Engineering
Indian Institute of Technology (Banaras Hindu University)
Varanasi – 221005 INDIA

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: *‘High temperature oxidation, metal dusting, erosion and corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel’*

Name of the Student: Sharvan Kumar

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the ***DOCTOR OF PHILOSOPHY.***

Date:

Place: Indian Institute of Technology (BHU), Varanasi

(Sharvan Kumar)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author’s personal use provided that the source and the institute’s copyright notice are indicated.

ACKNOWLEDGEMENT

I am very grateful and in debt to my supervisor Dr. G.S. Mahobia for his consistent help, encouragement, valuable discussions, and also the faith in me during the entire period of my research work. I would not have been able to complete the thesis without his utmost involvement and invaluable efforts. He motivated me to pursue research problems and the need for persistent effort to accomplish the goal. I am truly indebted to him. He is the real definition of the best teacher being friendly and behind for all problems of not only mine but all students.

Besides my supervisors, I would like to thank RPEC members: Prof. R.K.Gautam and Prof K. K. Singh (DPGC Member) for their insightful comments and encouragement.

I sincerely thank Prof. Sunil Mohan, Head of the Department of Metallurgical Engineering, and the former Heads Prof. N. K. Mukhopadhyay and Prof. R. K. Mandal for providing all the research facilities to accomplish my research in the Department.

My special thanks go to Prof. Vakil Singh, Emeritus Faculty, Department of Metallurgical Engineering IIT (BHU), who taught me a lot to convert the present work into the shape of thesis.

I am also thankful to Prof. T. R. Mankhand, Prof. N. C. Santhi Srinivas, Prof. B.N. Sharma, Prof. O.P. Sinha, Dr. R. Manna, Dr. K. Chattopadhyay, Dr. J. K. Singh, Dr. Vikas Jindal, Dr. C.K. Behera, Dr. Sudipta Patra, and all the faculty members for their valuable suggestion as well as teaching during course work.

I am also grateful to all the teachers for their continuous support during the entire period.

I am thankful to my all seniors/juniors and friends Dhananjay Pradhan, Raj Kumar Dishwar, Manish Kr Singh, Ankitendran Mishra, Ankit Singh, Subham Shaw, Aman Kumar Lal Das, Vinay Kumar Rai, Sankata Tiwari, Dheeraj Jaiswal, Debabrata Bhuiyan, Jaydeep Vishwakarma, Roop Chand Tandon, MD Rao, Amit Kumar Singh, Biswajit Mishra and Abhishek Shukla for their constant encouragement and making joyful and memorable moments at IIT (BHU), Varanasi.

I am also thankful to all the lab staff and workshop staff specially Shri Bal Govind Singh Ji, Shri Sashi Kant Pandey Ji, Shri Setu Ji, Shri Ashok Kumar Ji, Shri Lalit Kumar Singh, Shri Minz Ji, and all the office staff. I would also like to extend my heartiest thanks to

Acknowledgement

Prof. Rajiv Prakash (Prof.-in-charge, CIFC) and his technical team especially Mr. Girish Sahu for providing the research facilities.

Last, but not least, I would like to express my deepest gratitude to my family, my parents Mrs. Kamlesh and Mr. Ram Dev, for giving my life in the first place, for educating me, for their unconditional support and encouragement to pursue my interest.

I also wish to thank all my friends and the person whose names have not been mentioned in this piece of paper for extending their co-operation directly or indirectly.

(Sharvan Kumar)

Dedicated
To
My Beloved Parents

Table of Content

	Page No.
List of Figures	v
List of Tables	xi
List of Symbols	xiii
Preface	xv
Chapter-1 Introduction and Literature Survey	1
1.1 Introduction	1
1.2 Why nitrogen instead of nickel in austenitic stainless steel?	2
1.3 Development of Nickel Free Austenitic Stainless Steel	4
1.3.1 Role of Alloying Elements	5
1.3.2 Phases in High Nitrogen Austenitic Stainless Steel	7
1.3.3 Production Route	8
1.4 Applications of Fe-Cr-Mn-N Alloys	9
1.4.1 Biomedical Applications	10
1.4.2 Other Applications	12
1.5 High Temperature Oxidation	13
1.5.1 Thermodynamics of Oxidation	14
1.5.2 Oxidation Kinetics	15
1.5.3 Oxidation of Fe-Cr-Mn-N Austenitic Stainless Steel	16
1.5.4 Oxidation Under Moist Air Environment	17
1.6 Metal Dusting	19
1.6.1 Thermodynamics of Metal dusting	19
1.6.2 Mechanism of Metal dusting	20
1.6.3 Metal Dusting of Various High Temperature Alloys	22
1.6.4 Role of Oxide Layer	23
1.7 Solid Particle Erosion	24
1.7.1 Effect of Erosion Parameters	25
1.7.2 Erosion of Austenitic Stainless Steel	28
1.8 Aqueous Corrosion	30
1.9 Motivation	32
1.10 Scope of Work	32
1.11 Objective of Work.	33
Chapter-2 Material and Methods	35
2.1 Introduction	37
2.2 Material	37

2.3 Experimental Methods	38
2.3.1 Oxidation Test	38
2.3.2 Metal Dusting	39
2.3.3 Solid Particle Erosion Test	42
2.3.4 Corrosion Test	44
2.4 Characterization Techniques	45
Chapter-3 Oxidation Behavior of Fe-18Cr-21Mn-0.65N Austenitic Stainless Steel	47
3.1. Introduction	49
3.2 Results	50
3.2.1 Visual Observation	50
3.2.2 Oxidation Kinetics	51
3.2.3 XRD Analysis	54
3.2.4 Morphology of Oxidized Surface and Cross section	55
3.2.5 Precipitation behavior	61
3.3 Discussion	64
3.3.1 Oxidation Behavior	64
3.3.2 Precipitation of Cr ₂ N	67
3.4 Conclusions	67
Chapter-4 Metal Dusting Behavior of Fe-18Cr-21Mn-0.65N Austenitic Stainless Steel	49
4.1. Introduction	71
4.2. Results	72
4.2.1 Visual Observation and Weight Gain Analysis	72
4.2.2 XRD Analysis	72
4.2.3 Surface Morphology	74
4.2.4 Cross Sectional Analysis	79
4.2.4.2 EPMA Analysis	83
4.3. Discussion	86
4.3.1 Regime I: Metal Dusting Features at 400-500°C	86
4.3.2 Regime II: Metal dusting cum Oxidation at 600-700°C	90
4.4. Conclusions	93
Chapter-5 Erosion Behavior of Fe-18Cr-21Mn-0.65N Austenitic Stainless Steel	95
5.1 Introduction	97
5.2. Results	98
5.2.1 Weight Loss Analysis	98
5.2.2 Erosion rate	100
5.2.3 Hardness Profile	100
5.2.4 Tensile Behavior	102
5.2.5 Surface Morphology	104
5.2.6 Cross Sectional Analysis	106

5.3. Discussion	108
5.3.1 Effect of Oxidation	109
5.3.2 Effect of Temperature	111
5.3.3 Effect of Impact Angle	113
5.4 Comparison with Literature	115
5.5 Conclusions	117
Chapter-6 Potentiodynamic Corrosion Behavior of Fe-18Cr-21Mn-0.65N Austenitic Stainless Steel	119
6.1 Introduction	121
6.2. Results	122
6.2.1 EIS analysis	122
6.2.2 Polarization Test	126
6.2.3 Surface layer analysis	127
6.3. Discussion	137
6.3.1 EIS Study	138
6.3.2 Potentiodynamic Polarization Test	138
6.3.3 Surface layer analysis	139
6.3.4 SEM-EDS analysis	142
6.3.5 Mechanism of Corrosion	144
6.4. Conclusions	146
Chapter-7 Summary and Suggestion for Future Work	149
7.1 Introduction	151
7.2 Summary	151
7.2.1 Oxidation Behavior	151
7.2.2 Metal Dusting	151
7.2.3 Solid Particle Erosion Behavior	152
7.2.4 Potentiodynamic Corrosion Behavior	152
7.3 Suggestions for Future Work:	153
References	155
Glossary of Words	169
Appendices	173
List of Publications	183

List of Figures

	Page No.
Figure 1.1: Schaeffler diagram.	5
Figure 1.2: Schematic representation of metal dusting mechanisms.	21
Figure 2.1 (a) Optical microstructure and (b) X-ray diffraction of Fe-18Cr-21Mn-0.65N austenitic stainless steel in solution annealed condition.	38
Figure 2.2: (a) Photograph of the oxidation test set up (b) inside view of two zone split tube furnace, and (c) Axis digital balance.	39
Figure 2.3: Experimental setup for metal dusting test.	41
Figure 2.4: Photograph of Ducom air jet erosion tester.	43
Figure 2.5: (a) SEM micrograph of alumina particles and (b) Particle size distribution of erodent particles (Al_2O_3).	44
Figure 2.6: Photograph of CorrTest electrochemical work station, with flat type corrosion cell.	44
Figure 3.1: Photographs of the samples oxidized at 400-700°C for 100 h in static and dynamic air.	50
Figure 3.2: ΔW vs time plots for oxidation at 400-700°C up to 100 h in (a) static air, (b) dynamic air-2 lpm, and (c) dynamic air-6 lpm.	51
Figure 3.3: ΔW^2 vs time plots for oxidation at 400° to 700°C up to 100 h in (a) static air, (b) dynamic air-2 lpm, and dynamic air-6 lpm.	52
Figure 3.4: Plots for determination of activation energy for oxidation at 400-700°C under Static and Dynamic air conditions.	53
Figure 3.5: XRD patterns of the oxidized Fe-18Cr-21Mn-0.65N austenitic stainless steel at 400-700°C, up to 100 h in (a) static air and (b) dynamic air (6 lpm).	54
Figure 3.6: SEM micrographs and elemental analysis of the Fe-18Cr-21Mn-0.65N austenitic stainless steel oxidized at (a)400, (b)500, (c)600, and (d)700 °C for 100 h in dynamic air (6 lpm).	56
Figure 3.7: SEM micrographs and elemental analysis of the Fe-18Cr-21Mn-0.65N austenitic stainless steel oxidized at (a) 400°C, (b)500°C, (c), 600°C and (d)700 °C up to 100 h in static air.	58

Figure 3.8: SEM-EDS point analysis of cross section of the Fe-18Cr-21Mn-0.65N austenitic stainless steel oxidized up to 100 h at different temperatures; (a, b) 400°C, (c, d) 500°C, (e, f) 600 °C and (g, h) 700 °C in dynamic-6lpm and static air.	60
Figure 3.9: EDS mapping of cross section of the Fe-18Cr-21Mn-0.65N austenitic stainless steel oxidized for 100h at: (a)400°C, (b)500°C, (c)600°C and (d)700°C in dynamic air-6 lpm.	60
Figure 3.10: EDS mapping of cross section of the, Fe-18Cr-21Mn-0.65N austenitic stainless steel oxidized for 100 h in static air at: (e)400°C, (f)500°C, (g)600°C and (h)700°C.	61
Figure 3.11: TEM bright field images (a, c, e, g) and corresponding diffraction patterns (b, d, f, h) of the samples exposed at 400, 500, 600, and 700°C respectively, up to 100 h.	63
Figure 3.12: TTT diagram of the Fe-18 Cr-21 Mn-0.65 N austenitic stainless steel calculated using J-Mat Pro software.	63
Figure 3.13: Schematic of oxidation mechanism in (a) static and (b) dynamic air at 500-700°C.	66
Figure 4.1: Photographs of metal dusted coupons exposed for 300 h at (a) 400°C, (b) 500°C, (c) 600°C and (d) 700°C.	72
Figure 4.2: Plots, resulting from exposure of 300 h (a) weight gain vs time and (b) carbon deposited with respect to temperature.	72
Figure 4.3: XRD patterns of (a) metal dusted coupons exposed at 400°C, 500°C, 600°C, and 700°C (b) carbon deposited at the surface from 300 h of exposure at 400°C and 500°C.	73
Figure 4.4: SEM micrographs and corresponding EDS of (a) carbon deposited region; (b) area of less deposition of carbon; (c) carbon filaments showing branched structure; (d) fragmented particle and (e) pits formation at the surface after carbon removal on metal dusted coupon exposed at 400°C for 300 h.	75
Figure 4.5: SEM micrographs and corresponding EDS of (a) carbon deposited region; (b) area of less deposition of carbon; (c) globular structure containing carbon filaments and (d) surface showing formation of pits on metal dusted coupon exposed at 500°C for 300 h.	77

- Figure 4.6:** SEM micrographs and corresponding EDS of (a) oxide layer formed at the surface, (b) magnified image of the selected area (red rectangle) showing crystal formation of metal dusted coupon exposed at 600°C for 300 h. 78
- Figure 4.7:** SEM micrographs and corresponding EDS of metal dusted coupon exposed at 700°C for 300 h: (a) morphology of oxide layer formed at the surface, (b) magnified image of the selected area (red rectangle) showing needle-like structure formation. 79
- Figure 4.8:** SEM micrographs and corresponding EDS of (a) cross-section of metal dusted coupon exposed at 400°C for 300 h showing carbon deposition in filament form, (b) BSE micrograph showing pit depth. 80
- Figure 4.9:** SEM micrographs and corresponding EDS of (a) cross-section of metal dusted coupon exposed at 500°C for 300 h showing carbon deposition in filament form, (b) BSE micrograph showing pit depth. 81
- Figure 4.10:** SEM-BSE micrograph and EDS analysis showing two-layered structure of oxide scale and oxide/carbide region of metal dusted coupon exposed at 600°C for 300 h. 82
- Figure 4.11:** SEM-BSE micrograph and EDS analysis showing two-layered structure of oxide scale and oxide/ carbide region in the metal dusted coupon exposed at 700°C for 300 h. 83
- Figure 4.12:** EPMA area mapping of metal dusted coupon exposed for 300 h at (a) 400, (b) 500, (c) 600, and (d) 700°C respectively. 85
- Figure 4.13:** Schematic diagram showing mechanism of metal dusting from exposure at 400 and 500°C. 89
- Figure 4.14:** Schematic diagram showing the mechanism of metal dusting from exposure at 600 and 700°C. 93
- Figure 5.1:** Weight loss vs time plots of Fe-18Cr-21Mn-0.65N austenitic stainless steel eroded at (a) RT, (b) 400°C, (c) 500°C, (d) 600°C and (e) 700°C at three impact angles of 60°, 75° and 90°, solution treated, pre-exposed at respective temperatures of erosion, from RT to 700°C. 99

Figure 5.2: Plots showing erosion behavior of the Fe-18Cr-21Mn-0.65N austenitic stainless steel: (a) erosion rate vs temperature, (b) erosion rate vs angle of impact.	100
Figure 5.3: Microhardness vs depth plot of Fe-18Cr-21Mn-0.65N austenitic stainless steel eroded at (a) room temperature, (b) 400°C, (c) 500°C, (d) 600°C and (e) 700°C.	101
Figure 5.4: Tensile behavior of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, solution treated and pre exposed from 400°C to 700°C for 100 h, and tested at the respective temperature of pre-exposure: (a) engineering stress strain curves and (b) true stress strain plots.	103
Figure 5.5: SEM micrographs of the areas of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, eroded at: room temperature, 400°C, 500°C, 600°C and 700°C.	104
Figure 5.6: SEM micrographs of cross section of eroded scar showing the eroded crater profile of 18Cr-21Mn-0.65N-Fe austenitic stainless steel at RT, 400°C, 500°C, 600°C and 700°C.	106
Figure 5.7: SEM micrographs of cross section of areas of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, eroded at: room temperature, 400°C, 500°C, 600°C and 700°C.	108
Figure 5.8: XRD pattern of the Fe-18Cr-21Mn-0.65N austenitic stainless steel exposed at different temperature during erosion test.	109
Figure 5.9: BSE images of cross section of the Fe-18Cr-21Mn-0.65N austenitic stainless steel pre oxidized for 100 h (a) 600°C and (b) 700°C.	110
Figure 5.10: Schematic diagrams showing mechanism of erosion of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, at impact angles of (a) 60°, 75°, and (b) 90° at 600 and 700°C.	110
Figure 6.1: (a) Nyquist and (b, c) Bode plots of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples, unexposed and exposed for 100 h at 400-700°C.	123
Figure 6.2: Equivalent circuit diagram used for fitting EIS data of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples unexposed and exposed at 400-700°C for 100 h.	124

- Figure 6.3:** Potentiodynamic polarization plots of the Fe-18Cr-21Mn-0.65N austenitic stainless steel samples: (a) unexposed, and exposed at (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C for varying duration. 125
- Figure 6.4:** XRD patterns of the unexposed sample and the samples exposed at 400-700°C for 100 h. 128
- Figure 6.5:** XPS plots of Mn 2p_{3/2} after polarization test of the Fe-18Cr-21Mn-0.65N austenitic stainless steel samples (a) unexposed, and exposed for 100h at (b) 400°C, (c) 500°C (d) 600°C and (e) 700°C. 129
- Figure 6.6:** XPS plots of Fe 2p_{3/2} after polarization of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples (a) unexposed and exposed at (b) 400°C, (c) 500°C (d) 600°C and (e) 700°C for 100 h. 130
- Figure 6.7:** XPS plots of Cr 2p_{3/2} after polarization test of the Fe-18Cr-21Mn-0.65N austenitic stainless steel samples (a) unexposed, and exposed at (b) 400°C, (c) 500°C (d) 600°C and (e) 700°C for 100 h. 131
- Figure 6.8:** XPS plots of O 1s after polarization test of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples (a) unexposed and those exposed at (b) 400°C, (c) 500°C (d) 600°C and (e) 700°C for 100 h. 132
- Figure 6.9:** SEM-EDS analysis of corroded surface of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples, (a) unexposed and those exposed at (b) 400°C, (c) 500°C (d) 600°C, (e&f) 700°C for 100 h. 134
- Figure 6.10:** SEM micrographs of longitudinal cross sections, normal to corroded surfaces of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, (a) unexposed and exposed for 100 h: at (b) 400°C, (c) 500°C (d) 600°C and (e) 700°C. 137
- Figure 6.11:** SEM micrographs of surface of the Fe-18Cr-21Mn-0.65N austenitic stainless-steel samples exposed for 100 h at: (a) 600°C and (b) 700°C. 137
- Figure 6.12:** Schematic mechanism of corrosion for the Fe-18Cr-21Mn-0.65N austenitic stainless steel samples, (a) unexposed, and exposed at 400-500°C, (b) exposed at 600-700°C for 100 h. 145

List of Tables

	Page No.
Table 1.1: Comparison of mechanical properties of different austenitic stainless steels.	3
Table 2.1: Carbon activity and partial pressure of oxygen at corresponding temperature.	40
Table 2.2: Physical properties of aluminum oxide (Al ₂ O ₃) erodent.	42
Table 2.3: Operating conditions for solid particle erosion test.	43
Table 3.1: Values of exponent 'n'.	52
Table 3.2: Weight gain per unit area (ΔW) and parabolic rate constant (k_p).	53
Table 3.3: Phases formed at different temperatures, characterized by XRD.	54
Table 3.4: Diffusion coefficient of cations through chromia layer.	65
Table 4.1: Phases identified by XRD analysis after metal dusting process at different temperatures.	73
Table 4. 2: Gibbs free energy (kcal/mol K ⁻¹) of formation of various carbides and oxides.	87
Table 5.1. Erosion rate (ER) at different impact angles and temperatures.	99
Table 5.2: Tensile properties of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, solution treated and exposed from 400°C to 700°C for 100 h, and tested at the respective temperature of pre-exposure.	103
Table 5. 3: Bulk hardness of the Fe-18Cr-21Mn-0.65N austenitic stainless-steel specimens of cross section, from the center region at room temperature, solution treated and exposed from 400°C to 700°C for 100 h, eroded at the respective temperature of pre-exposure.	103
Table 5.4: Strain hardening and strength coefficient of the Fe-18Cr-21Mn-0.65N austenitic stainless steel, solution treated and exposed from 400 to 700°C for 100 h and tested at the respective temperature of pre-exposure.	103
Table 5.5: Effect of the angle of impact on the depth of erosion scar after erosion at RT, 400, 500, 600 and 700°C.	114
Table 5.6. Comparison of erosion rate of various nickel containing austenitic stainless steels.	116

Table 6.1: Electrochemical impedance spectroscopy (EIS) fitted parameters of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples unexposed and exposed at 400-700°C.	123
Table 6.2: Polarization test parameters of Fe-18Cr-21Mn-0.65N austenitic stainless steel samples unexposed and exposed at 400-700°C for different time intervals.	124

List of Symbols

wt. %	Weight percentage
μm	Micro meter
ER	Erosion Rate
k_p	Parabolic rate constant
HV	Vicker's Hardness
MPa	Mega Pascal
MT	Metric tons
r_6	Octahedral radius
r_4	tetrahedral radius
$^{\circ}\text{C}$	Degree Centigrade
mm	Millimeter
V	Voltage
θ	Theta
kN	Kilo Newton
h	Hour
Sec	Second
min	Minute
mJ	milli Joule
a_c	activity of carbon

Abbreviations

SA	Static Air
DA	Dynamic Air
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
UTS	Ultimate Tensile Strength
YS	Yield Stress/Yield Strength
SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-ray Spectroscopy
BSE	Back Scattered Electron
XRD	X-ray Diffraction
XPS	X-ray photoelectron spectroscopy
EPMA	Electron probe microanalyzer
TEM	Transmission Electron Microscope
BF	Bright Field
DP	Diffraction Pattern
EIS	Electrochemical Spectroscopy
TTT	Time-Temperature-Transformation
CCT	Continuous Cooling Transformation
RT	Room Temperature
DBTT	Ductile to brittle transition temperature
CN	Coordination number
ASME	American Society of Mechanical Engineers
HCP	Hexagonal closed packed
T	Temperature
E_{corr}	Corrosion Potential
i_{corr}	Corrosion current
OCP	Open Circuit Potential
CR	Corrosion Rate

Preface

Nickel free or low nickel nitrogen and manganese stabilized austenitic stainless steels based on Fe-Cr-Mn-N alloy system are an important class of engineering material that exhibit a wide range of properties such as strength, toughness, high pitting corrosion resistance, and creep properties. Nitrogen and manganese alloying enhances the austenitic stability and work hardenability of this class of steel. The 200 series of austenitic stainless steel exhibit acceptable strength in the temperature range from cryogenic to higher temperature. Applications of conventional austenitic stainless steels such as 316L, S304, S310, etc. are restricted mainly due to the high cost of nickel. Fe-Cr-Mn-N class of alloys are well studied and documented for biocompatibility and other applications such as retainers' rings in power generators, drill collars of oil rigs, vessels of fusion bed reactors, and armor materials in the defence sector. In the nuclear industry, it is highly undesirable to use high nickel containing stainless steel because nickel in the steel undergoes activation by neutron radiation. This reduces ductility of the material in service and creates problems in the disposal of a component after decommissioning. In such applications, the Fe-Cr-Mn-N steel is cyclically exposed between 300-700°C. In several applications, this grade of stainless steel is welded with other low alloy steels and C-Mn steels, undergoes intermediate temperature exposure (400-700°C for 10-40 h) during stress relieving heat treatment. Austenitic stainless steel is widely used in heat exchangers and gas reforming units where it is exposed to intermediate temperature range from 300-500°C. Low temperature (400-500°C) stress relieving treatment of 8-10 h, is needed to remove peak stress and maintain dimensional stability during machining of stainless steel, which causes cyclic oxidation. Components such as transporting pipes which are used to transport a reducing gas mixture of CO and H₂ suffer from carbon corrosion. These components get eroded with time due to the impingement of sand particles inside the gas on the interior of

the pipes. Cl ions are inevitable in various industries such as fossil, food, paper, and chemical. Stainless steel components have been widely used in such industries and are exposed to sea water environment in the coastal region.

In the present work, high temperature oxidation, metal dusting, erosion, and corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel, with a negligible amount of nickel (present as impurity, derived from the raw materials used in steel making) has been studied in the temperature range of 400-700°C. This thesis is divided into seven chapters and the details of each chapter are given below:

Chapter-1 presents a brief introduction of high manganese nitrogen stabilized austenitic stainless steels. This chapter describes the role of alloying elements and the physical metallurgy of nitrogen and manganese alloyed austenitic stainless steel. An extensive literature survey has been made on the oxidation, metal dusting, erosion, and corrosion behavior of high manganese nitrogen stabilized austenitic stainless steel. The gaps were identified from the literature. The scope and objectives of the present research work are described.

Chapter-2 deals with material and methods of oxidation, metal dusting, erosion, and corrosion tests. The initial characterization of the material, such as optical microscopy and mechanical properties are included in this chapter. This chapter also comprises the details of the experimental setup used in different experimental work and characterization techniques used in the present study.

Chapter-3- deals with the cyclic oxidation behavior of nitrogen and manganese stabilized austenitic stainless steel (Fe-18Cr-21Mn-0.65N) from 400-700°C up to 100 h. The effect of moist airflow on oxidation behavior from 400-700°C was systematically studied gravimetrically and the oxidized surfaces were characterized using SEM-EDS and XRD.

During oxidation, Mn diffused out from the matrix to surface and reacted with the oxygen associated with the passive chromia layer and formed nonprotective Mn_2O_3 and spinel of the oxides of Fe, Cr, and Mn. At 700°C, there was rapid vaporization of Cr and consequent reduction in weight gain in dynamic air (DA) as compared with that in static air (SA). Precipitation of Cr_2N of different morphology was established through TEM analysis. The rate of oxidation increased with a rise in temperature in both the conditions. The high diffusion coefficient of Mn through the chromia layer was the key factor in lowering the oxidation resistance of this steel. Oxidation from 500-700°C resulted in the formation of a duplex oxide layer with Mn oxide at the top and spinel $CrFeMnO_4$, Fe_2MnO_4 , $FeMn_2O_4$, at the bottom. Evaporation of Cr due to the formation of volatile $CrO_2(OH)_2$ at 700°C, decreased the weight gain in humid dynamic air condition as compared to that in static air. TEM study showed cellular precipitation of HCP chromium nitride (Cr_2N) at 600 and 700°C while at 500°C faceted globular morphology was observed. Precipitation of the detrimental σ phase was not observed in this study.

Chapter-4 presents the features of metal dusting of Fe-18Cr-21Mn-0.65N in syngas environment (75% H_2 and 25 % CO) at 400-700°C, under cyclic exposure for 300 h. Study reveals carbon corrosion at 400-500°C, however, at 600-700°C, oxidation of Mn and formation of Mn-Cr-O spinel significantly reduced the carbon attack. The surface and cross section of the exposed coupons were examined by XRD, SEM-EDS, and EPMA. Metal dusting resulted in formation of very few corrosion pits of the size 2-7 μ m and epitaxial growth of carbon nanotubes on the surface exposed at 400-500°C. Extensive growth of carbon filaments was found from 400-500°C due to the high activity of carbon. The limited metal dusting (carbon erosion) of metal particles showed formation of a few shallow pits. Metal dust comprising of graphite, Mn, and Fe along with fragmented metal carbide particles formed from low temperature exposure. At high temperature of 600-700°C rapid

diffusion of Mn resulted in the formation of a thick porous layer of Mn oxide and that inhibited the growth of carbon filaments. This was followed by an intermediate layer of spinel of Mn, Cr, and O. The presence of a few metal carbides/oxides showed that initially the process started with carburization reaction but later oxidation of these carbides took place. In short, the alloy exhibited Type III mechanism of metal dusting where initially formed metastable carbides were selectively oxidized, depending upon the activity of carbon.

Chapter 5 presents high temperature erosion behavior of high manganese nitrogen stabilized austenitic stainless steel, exposed at 400-700°C for 100h, at three different impingement angles of 60°, 75° and 90°. Acicular alumina was used as an erodent with a discharge rate of 4.6±0.5 gm/min. Optical microscopy, Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) were used to characterize the eroded surface. Tensile testing and microhardness evaluation was also carried out for better understanding of the erosion behavior. Erosion rate increased with rise in temperature of exposure and was found to be associated with decrease in tensile strength and hardness of the steel. Oxidation at high temperature during pre-exposure, played an important role in accelerating the erosion rate, particularly at 600 and 700°C.

Oxidation of the alloy, during exposure, produced brittle oxide scale, composed of spinel of Mn, Cr, and O. Pre-exposure at higher temperature caused precipitation of Cr₂N, that reduced tensile strength and hardness of the alloy. High velocity impact of alumina particles caused breakage of brittle oxide layer and directly eroded the base material. Rise in temperature caused increase in erosion rate at all impingement angles. As the angle of impingement increased from 60° to 90°, erosion rate decreased at 600 and 700°C due to the formation of soft ferrite at the surface, below the oxide layer. The changes in hardness were highest at 90° of impingement angle at all temperatures and the erosion rate was lowest. It

is attributed to higher plastic deformation and reduced velocity of the incoming particle by rebounding interaction. The mechanism of erosion was ploughing/cutting, lip formation at a lower angle of impingement, delamination and crater/pit formation at normal angle, at all temperatures.

Chapter 6 deals with corrosion behavior of Fe-18Cr-21Mn-0.65N austenitic stainless steel, pre-exposed at intermediate temperature from 400-700°C, for different time intervals, up to 100 h. Potentiodynamic polarization test was performed at room temperature in seawater environment (0.5M NaCl) to evaluate corrosion behavior of the steel samples pre-exposed at different temperatures. Polarization test shows that an increase in the temperature of exposure, reduced the corrosion resistance of the steel. EIS study of the passive layer formed also showed a decreasing trend in corrosion resistance of the passive film. The corroded surface of the sample was characterized by X-ray photoelectron spectroscopy (XPS) and Scanning electron microscopy (SEM-EDS). XPS analysis revealed oxides and hydroxide of Cr^{+3} , Mn^{+3} , and Fe^{+3} . Higher temperatures of exposure favored formation of manganese hydroxide. Pitting mechanism was prominent in the specimens exposed from room temperature to 500°C, whereas there was a mixed mode of corrosion (intergranular combined with accelerated pitting) in the specimens exposed at higher temperatures of 600 and 700°C. Precipitation of Cr_2N along grain boundaries and within the matrix was found to be the main cause of the accelerated corrosion attack.

Chapter 7 presents the overall summary of the present investigation, including important conclusions and scope of the future work.