

**VANADIUM RECOVERY IN THE ELECTRO-
ALUMINOTHERMIC PRODUCTION OF
FERROVANADIUM.**

deur

Matthys Karel Gerhardus Vermaak

Voorgelê ter vervulling van 'n deel van die vereistes vir die graad

Magister in Ingenieurswese

in die Departement van Materiaalkunde en Metallurgiese
Ingenieurswese, Universiteit van Pretoria, Pretoria, Republiek van
Suid-Afrika.

Projekleier : Professor P.C. Pistorius

Januarie, 2000

Aan Ilse met liefde.

ACKNOWLEDGEMENTS

I would like to thank and herewith express my sincere appreciation to the following people and institutes:

- Prof. Chris Pistorius, my supervisor, for guidance and continuous support.
- S. Havenga for all her support.
- Eben Bernardo and A. Brugman, for appreciating the need for this research and the opportunity.
- Highveld Steel and Vanadium Corporation Limited for financial support.
- Department of Material Science and Metallurgical Engineering, Pretoria University, for facilities.
- S. Verryn and M. Loubser of the Geology Department for help in various analyses.
- A. Botha of the Electron-microscopy section for assistance and thrust bestowed upon me to use the electron-microscope after-hours.
- R. Muir, for manufacture and repair of countless special glassware equipment.
- My father, mother, Leslie, Pieter, Batsie, Ilse and her parents, Muller and other friends for their, prayers, continuous support and patience throughout.
- My fellow graduate students, Rian, Giel, Josè, Michelle, Niel, Riaan, Ferdus, Colette, Nana, Daudet and Alain for their support and advice.
- The Lord, for the abilities He gave me and the opportunities to develop them.

SOLI DEO GLORIA

VANADIUM RECOVERY IN THE ELECTRO-ALUMINOTHERMIC PRODUCTION OF FERROVANADIUM.

by

Matthys Karel Gerhardus Vermaak

Prof. P.C. Pistorius

Department of Material Science and Metallurgical Engineering

Master Degree in Engineering

Abstract.

Ferrovandium is sometimes produced from V_2O_3 in electric arc furnaces, using aluminium as reductant. CaO fluxes the alumina which forms during reduction of the vanadium oxide. Vanadium recovery in the electro-aluminothermic process is mainly controlled by losses to the slag. These include metal droplet entrainment (these droplets remain in the slag after solidification) and unreduced vanadium oxides in the slag. Both these factors might be a significant cause of vanadium losses.

To quantify factors which can affect the equilibrium vanadium loss, the vanadium oxide activity coefficient was measured experimentally for different slag compositions. Hydrogen-water mixtures were used to control the partial oxygen pressure (ca. 10^{-13} atm) over CaO- Al_2O_3 slags contained in vanadium crucibles at 1700°C; gas phase mass transfer was controlled by jetting the gas mixture onto the slag surface. Manipulation of the redox conditions at a single slag composition and temperature showed that – as expected – the vanadium is present in the trivalent state in the slag. The slag basicity (CaO/ Al_2O_3 ratio) was found to have a very strong effect on the activity coefficient of $VO_{1.5}$, with clear implications for the effect of plant practice on vanadium loss. The laboratory equilibrium results were compared to EDX analyses obtained from actual industrial slag samples. Analysis of the industrial slags indicate that slags with higher Al_2O_3 contents clearly have lower vanadium oxide contents.

An alteration of the slag composition by adding less CaO will lower the soluble vanadium loss, inevitably changing the separation of the solid ferrovandium phase from the slag phase. The effect of slag basicity on metal droplet entrainment was assessed by

investigating solidified slag samples. The effect of droplet entrainment on vanadium loss could not be fully quantified due to the strong segregation behavior and crowding close to the slag-metal surface. Samples which were taken close to this interface showed unusually high vanadium losses, compared to samples taken at the top of the bulk slag sample.

Equilibrium calculations were also performed to predict the relative influence of temperature, MgO content of the slag, and aluminium content of the ferrovanadium on oxidic vanadium loss. The activity-composition relations for the species in the slag and ferrovanadium were estimated using the Chemsage software package. The lower predicted vanadium content of the slag compared to industry is probably the result of uncertainties regarding the aluminium activity. Nevertheless, lower MgO contents of the slag, higher aluminium contents of the ferrovanadium and lower tap temperatures will yield lower vanadium oxide losses to the slag.

Keywords: Key Words: electro-aluminothermic process, ferrovanadium, vanadium, activity coefficient, slag-metal equilibrium, basicity, slag losses, metal droplet entrainment.

VANADIUMHERWINNING IN DIE ELEKTRO-ALUMINOTERMIESE PRODUKSIE VAN FERROVANADIUM

deur

Matthys Karel Gerhardus Vermaak

Prof. P.C. Pistorius

Departement Materiaalkunde en Metallurgiese Ingenieurswese

Meestersgraad in Ingenieurswese

Opsomming

Ferrovandium word soms van V_2O_3 in 'n elektriese boogooand vervaardig, met aluminium as reduktant. CaO dien as vloeimiddel vir die alumina wat gevorm word tydens die reduksie van die vandiumoksied. Vandiumherwinning in die elektro-aluminotermiese proses word hoofsaaklik deur metaaldruppelvasvang (die druppels bly vasgevang in die slak nadat stolling plaasgevind het) en ongereduseerde vandiumoksied in die slak beheer. Beide die meganismes is moontlik verantwoordelik vir beduidende vandiumverliese.

Faktore wat die ewewigvandiumverliese kan beïnvloed, kan gekwantifiseer word deur die vandiumoksiedaktiwiteitskoeffisiënt eksperimenteel, vir verskillende slaksamestellings, te bepaal. Water-waterstofgasmengsels is gebruik om die parsieë suurstofdruk (ca. 10^{-13} atm) by 1700°C oor CaO- Al_2O_3 slakke wat in suiwer vandiumkroese geplaas is, te beheer. Gasmassa-oordrag is beheer deur die gasmengsel direk op die slakoppervlakte te spuit. Verandering van die redokstoestande vir 'n enkele slaksamestelling en temperatuur toon, soos verwag, dat V^{3+} die stabiele oksidasietoestand is. Dit is bevind dat die slakbasisiteit (CaO/ Al_2O_3 -verhouding) 'n baie sterk invloed op die vandiumoksiedaktiwiteitskoeffisiënt ($\text{VO}_{1,5}$) het, met duidelike implikasies vir die aanlegpraktyk ten opsigte van vandiumverliese. Die laboratoriumewewigsresultate is toe met EDS analises van industriële slakke vergelyk. Die analises toon aan dat slakke met 'n laer alumina-inhoud laer vandiumoksiedvlakke het.

'n Wysiging van die slaksamestelling deur minder CaO by te voeg, sal vandiumoksiedverliese verlaag, maar die skeidingsgedrag van die vaste ferrovandiumfase sal noodwendig ook verander. Die effek van slakbasisiteit op

metaaldruppelvasvanging is aangespreek deur industriële slakke te ondersoek. Die effek van slakbasisiteit kon nie ten volle gekwantifiseer word nie weens die sterk segregasiegedrag en die versameling van die metaaldruppels naby die slak-metaalintervlak. Monsters wat in die omgewing van die interval geneem is, het ongewoon hoë vanadiumverliese getoon vergeleke met monsters wat aan die bokant van die blokslakmonster geneem is.

Die relatiewe invloed van die MgO-inhoud van die slak, die aluminiuminhoud van ferrovanadium en die taptemperatuur is voorspel deur ewewigsberekeninge uit te voer. Die beraamde samestelling-aktiwiteitsverwantskappe van die spesies in ferrovanadium en in die slak is verkry deur van die Chemsage sagtewarepakket gebruik te maak. Die laer voorspelde vanadiumoksiedinhoud van die slak vergeleke met aanlegdata is toe te skryf aan onsekerhede wat betref die aluminiumaktiwiteit. Ten spyte hiervan, sal laer MgO-vlakke in die slak, hoër aluminiumvlakke en laer taptemperature die vanadiumopbrengs verhoog.

Sleutelwoorde: elektro-aluminotermiese proses, ferrovanadium, vanadium, aktiwiteitskoëffisiënt, slak-metaalewewig, basisiteit, slakverliese, metaaldruppelvasvanging.

Table of contents

1.Literature study	1
1.1. Introduction	1
1.2. Production of ferrovanadium	1
1.2.1. Introduction	1
1.2.2. Carbon reduction	2
1.2.3. Silicon reduction	4
1.2.4. Aluminium reduction	4
1.2.4.1. Reduction of vanadium oxides	4
1.2.4.2. Aluminothermic reduction	5
1.2.4.3. Electro-aluminothermic production of ferrovanadium	9
1.2.4.4. Factors influencing vanadium recovery in the electro-aluminothermic production of ferrovanadium	15
1.2.4.4.1. The loss of vanadium reverts due to theft	15
1.2.4.4.2. Loss of vanadium units as oxide spillages during handling and transportation	15
1.2.4.4.3. Loss of vanadium units as reverts	16
1.2.4.4.4. Metal droplet entrainment	16
1.2.4.4.4.1. Influence of the physicochemical properties of the slag on the separation of the solid phase	19
1.2.4.4.5. Vanadium loss due to unreduced oxides in the high-alumina slag	26
1.3. Thermodynamic properties	27
1.3.1. Behavior of systems similar to the vanadium systems	27
1.3.2. Estimation of the partial oxygen pressures in the industrial ferrovanadium production process.	29

1.4. Research problem and objectives	35
1.5. Investigation into experimental techniques and procedures	36
1.5.1. Evaluation of different gas mixing systems	36
1.5.2. Experimental evaporation technique and procedure	38
1.5.3. Kinetics of the vanadium oxidation reaction	44
1.6. Conclusion	50
2. Experimental techniques	51
2.1. Introduction	51
2.2. Experimental set-up	51
2.2.1. Gas system set-up	51
2.2.2. The furnace set-up	66
2.2.3. Quenching set-up	71
2.2.4. Crucibles	73
2.3. Experimental procedure	74
2.3.1. Slag preparation	74
2.3.2. Experimental run	76
2.3.3. Sample analysis	76
3. Equilibrium time determination	81
4. Results and discussion	84
4.1. Activity coefficient relations	84
5. Industrial slag sample investigations	92
5.1. Introduction	92
5.2. Oxidic phase analysis	92
5.2.1. Experimental procedure	92
5.2.1.1. Sample preparation	92

5.2.2. Results and discussion	94
5.2.2.1. Oxidic phase investigations	94
5.2.2.2. Composition relations of the oxidic phase	100
5.2.2.3. Industrial slag sampling	102
5.2.2.4. Industrial X.R.F. relations	105
5.3. Metallic phase analysis	108
5.3.1. Introduction	108
5.3.2. Experimental procedure	108
5.3.2.1. Sample preparation	108
5.3.2.2. Procedure to determine droplet-size distributions and to estimate the mass of vanadium associated with the metallic phase	108
5.3.3. Results and discussion	110
6. Equilibrium simulation calculations	120
6.1. Introduction	120
6.2. Results and discussion	120
7. Conclusion	132
8. Recommendations for future work	134
9. References	135
Appendices	139
Appendix 1	139
Appendix 2 : EDX analysis of experimental slags	140
Appendix 3. Industrial slag analysis	147
Appendix 4. Summary of slag analysis	162
Appendix 5. Metal droplet analysis of dipped sample	163
Appendix 6. Chemical composition of dipped sample	165

Appendix 7. Metal droplet analysis	166
Appendix 8. Estimated activity data of species in the CaO-Al ₂ O ₃ system	170
Appendix 9. Estimated activity data of MgO in the CaO-Al ₂ O ₃ -MgO system	171
Appendix 10. Estimated activity data of Al ₂ O ₃ in the CaO-Al ₂ O ₃ -MgO system	172
Appendix 11. Estimated activity data of Al ₂ O ₃ in the CaO-Al ₂ O ₃ -MgO system	175
Appendix 12. Estimated activity data of Al and V in the FeV system	177
Appendix 13. Estimated activity data of Al and V in the FeV system	179