VANADIUM RECOVERY IN THE ELECTRO-ALUMINOTHERMIC PRODUCTION OF FERROVANADIUM.

deur

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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.

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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. Loubscher 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

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Abstract.

Ferrovanadium 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 ferrovanadium 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

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Opsomming

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

Faktore wat die ewewigvanadiumverliese kan beïnvloed, kan gekwantifiseer word deur die vanadiumoksiedaktiwiteitskoëffisiënt eksperimenteel, vir verskillende slaksamestellings, te bepaal. Water-waterstofgasmengsels is gebruik om die parsiële suurstofdruk (ca. 10^{-13} atm) by 1700°C oor $CaO\text{-}Al_2O_3$ slakke wat in suiwer vanadiumkroese 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 vanadiumoksiedaktiwiteitskoëffisiënt ($VO_{1.5}$) het, met duidelike implikasies vir die aanlegpraktyk ten opsigte van vanadiumverliese. Die laboratoriumewewigsresultate is toe met EDS analises van industriële slakke vergelyk. Die analises toon aan dat slakke met 'n laer alumina-inhoud laer vanadiumoksiedvlakke het.

'n Wysiging van die slaksamestelling deur minder CaO by te voeg, sal vanadiumoksiedverliese verlaag, maar die skeidingsgedrag van die vaste ferrovanadiumfase 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 intervlak 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.

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