HIGH TEMPERATURE PHASE RELATIONS IN THE TiO_X-FeO_Y-VO_Z SYSTEM

by

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Summary

The minerals rutile (TiO_2) and ilmenite ($FeTiO_3$) are used as raw materials in the production of titanium oxide pigments. The two main processing routes are the sulphate and the chloride processes. Over the last four decades the trend has been to produce more titanium dioxide pigment via the chlorination process. TiO_2-rich slag, produced by carbothermic reduction of ilmenite, is used as feed material to the chlorination process. One of the quality specifications on the slag is that the vanadium content, expressed as $\%V_2O_5$, be less than 0.6% V_2O_5. Approximately 10% FeO is retained in the slag for fluxing purposes. From the standard free energies of formation of vanadium and iron oxides all of the FeO would first have to be reduced before vanadium oxide will be reduced into the metal if all species are present at unit activity. However, when mixtures of elements in the metal, and oxides in the slag are considered some vanadium may be recovered to the metal. The activity-composition behaviour of vanadium oxide in high TiO_2 slags is not known. Before the activity of vanadium oxide can be determined phase relations within the TiO_X-FeO_Y-VO_Z system, at the high TiO_X side, should be known. In this study phase relations within the two pseudo-binary systems FeO-V_2O_3 and TiO_2-V_2O_3 at 1400 °C, 1500 °C and 1600 °C at partial oxygen pressures of 3.02×10^{-10} atm, 2.99×10^{-9} atm and 2.31×10^{-8} atm respectively were determined with the quench technique. Analysis techniques used in determining the phase relations within the reacted samples were X-ray diffraction, Electronprobe microanalysis (Energy dispersive spectrometry and Wavelength dispersive spectrometry), and optical microscopy. The V_2O_3-TiO_2 pseudo-binary phase diagram contains the solid solution phases M_2O_3, M_3O_5 and higher Magneli phases (M_nO_{2n-1}) with M=(V, Ti). In these solid solution phases V^{4+} substitute for Ti^{4+}, and V^{3+} substitute for Ti^{3+}. The V_2O_3-FeO pseudo-binary phase diagram consists of the solid solution phases M_2O_3 and M_3O_4, as well as liquid, M=(V, Fe). In the M_2O_3 and M_3O_4 solid solution phases V^{3+}, Fe^{3+} and Fe^{2+} can substitute for each other. This work is a first step in determining the activity-composition behaviour of vanadium oxide in high TiO_2 slag.

Opsomming

Die minerale rutiel (TiO_2) en ilmeniet ($FeTiO_3$) word as roumateriaal in die produksie van titaandioksiedpigment gebruik. Hoofsaaklik twee prosesse, die sulfaatproses en die chlorineringsproses, word gebruik. Die neiging oor die afgelope vier dekades was om meer titaandioksiedpigment via die chlorineringsproses te produseer. TiO_2-ryke slak, geproduseer

titaandioksiedpigment via die chlorineringsproses te produseer. TiO_2-ryke slak, geproduseer deur die karbotermiese reduksie van ilmeniet, word gebruik as toevoermateriaal tot die chlorineringsproses. Een van die gehaltespesifikasies vir die slak is dat die vanadiuminhoud, uitgedruk as %V_2O_5, minder as 0.6% V_2O_5 moet wees. Ongeveer 10% FeO word oorgehou in die slak ten einde die slak vloeibaar te maak. Die standaard vrye energie van vorming vir vanadium- en ysteroksiede toon aan dat al die FeO eers gereduseer moet word na die metaal alvorens vanadiumoksied gereduseer sal word, as alle spesies by eenheidsaktiwiteit is. Indien egter mengsels van elemente in die metaal, en oksiede in die slak beskou word, mag vanadium tog na die metaal herwinbaar wees. Die aktiwiteit-samestellingsgedrag van vanadiumoksied in TiO_2-ryke slak is nie bekend nie. Alvorens die aktiwiteit van vanadiumoksied bepaal kan word, moet die faseverwantskappe in die TiO_X-FeO_Y-VO_Z sisteem, aan die TiO_X kant, eers bekend wees. In hierdie werk is die faseverwantskappe in die pseudo-binêre sisteme FeO-V_2O_3 en TiO_2-V_2O_3 by 1400 °C, 1500 °C en 1600 °C by parsiële suurstofdrukke van 3.02×10^{-10} atm, 2.99×10^{-9} atm en 2.31×10^{-8} atm onderskeidelik bepaal deur van die afblustegniek gebruik te maak. Analisetegnieke gebruik om die faseverwantskappe in die gereageerde monsters te bepaal, was X-straal diffraksie, mikrosonde-analises (Energie gedisperseerde spektrometrie and Golflengte gedisperseerde spektrometrie), and optiese mikroskopie. Die V_2O_3-TiO_2 pseudo binêre fasediagram bevat die vaste oplossingsfases M_2O_3, M_3O_5 and hoër Magneli fases (M_nO_{2n-1}) met M=(V, Ti). In die kristalstruktuur van die vaste oplossingsfase word Ti^{4+} deur V^{4+} vervang, en Ti^{3+} word deur V^{3+} vervang. Die V_2O_3-FeO pseudo binêre fasediagram bevat die vaste oplossingsfases M_2O_3 en M_3O_4, asook vloeistof, M=(V, Fe). In die M_2O_3 en M_3O_4 vaste oplossingsfases kan V^{3+}, Fe^{3+} en Fe^{2+} mekaar onderling in die kristalstruktuur vervang. Hierdie werk is die eerste stap in die bepaling van die aktiwiteit-samestellingsgedrag van vanadiumoksied in TiO_2-ryke slak.

Key words

ilmenite, chloride process, vanadium oxide, phase relations, high TiO_2-slag, partial oxygen pressure, quench technique, equilibrium, pseudo-binary system, V_2O_3, FeO, TiO_2

Sleutelwoorde

ilmeniet, chloriedproses, vanadiumoksied, faseverwantskappe, TiO_2-ryke slak, parsiële suurstofdruk, afblustegniek, ewewig, pseudo binêre sisteem, V_2O_3, FeO, TiO_2

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