

https://dspace.org/

Hydrocarbon reduction of manganese ores

Bhalla, Amit

2018

https://hdl.handle.net/10539/25884

Bhalla, Amit (2018) Hydrocarbon reduction of manganese ores, University of the Witwatersrand, Johannesburg, https://hdl.handle.net/10539/25884.

Downloaded from a DSpace repository. https://dspace.org/

ABSTRACT

Reduction behavior of South African Mamatwan manganese ore using methane-argon-hydrogen gas mixture was investigated experimentally in the temperature range of 1050°C to 1250°C. The effect of changing gas mixture composition, time and temperature was studied using a vertical tube furnace. After each test, three representative samples were prepared; one was analyzed by chemical analysis to obtain metallization results as a function of each reducing condition for each time interval over the total reduction period of two hours. Second sample was analyzed by X-ray diffraction to determine the progress of phase changes; the third sample was mounted, polished and submitted for SEM-EDAX in order to examine the morphology of the ore and its changes in the course of reduction. It was seen that CH_4 was an effective reductant as it cracked, supplying the reaction site with hydrogen gas and very fine solid carbon. The excess carbon from cracking of methane ensures regeneration of reductants CO and H_2 from reaction product gases of CO_2 and H_2O ensuring low partial pressure of oxygen at the reaction site. Hydrogen gas may also be involved in the reduction of iron oxide components of the ore. Moreover, depending upon temperature and CH_4/H_2 ratio in the gas phase the activity of carbon in the system reaches values much higher than unity, shifting the reduction reaction by carbon to lower temperatures. It was observed that bulk of the metallization occurred in the first thirty to forty minutes and the metallization reached some kind of a reduction maximum at 73% metallization. The Mn/Fe ratios in the resulting alloy were higher than those in ordinary carbothermic solid-state reduction, indicating the simultaneous reduction of Fe and Mn at these low reducing temperatures due to a low oxygen potential set up by the methane bearing gas mixtures. It was seen that metallization of Mamatwan ore proceed in two stages. First, reduction of the higher oxides to MnO and metallic iron. Second, reduction of any remaining oxides and MnO to mixed carbide of iron and manganese. During first stage values of effective CO-CO_2 diffusivities generated by the model were found to lie in the range from $1.45 * 10^{-6}$ cm^2sec^{-1} to $8.43*10^{-6}$ cm^2sec^{-1} at 1100°C. Apparent activation energy for first stage calculated in the temperature range of 1050°C to 1250°C varied from 1.47 kJ/mol to 24.72 kJ/mol indicating possibility of diffusional control. For the second stage the experimental curves could be duplicated with the mathematical model reasonably well with a maximum difference between the experimental and predicted values being about 5 percent. Rate of metallization values during the second stage (Ms) changed between $1.83*10^{-8}$ $mol.sec^{-1}.cm^{-2}$ and $8.55*10^{-8}$ $mol.sec^{-1}.cm^{-2}$. Specific rate constant values (k_s) for the second stage, varied from $5.53*10^{-6}$ cm/sec to $3.16*10^{-5}$ cm/sec which are much smaller than specific rate constant for the first stage of reduction (k_f), which varied from $1.64*10^{-4}$ cm/sec to $1.15*10^{-4}$ cm/sec, as the rate of second stage of the reduction is much slower than the rate of the first stage. X ray analysis revealed that manganese ore was reduced primarily to carbide Mn_7C_3 at lower temperature range of the experiments, but at 1200°C the dominant reaction product was

Mn_5C_2 in both mixtures of methane-argon and methane-hydrogen. The S.E.M images revealed that the product metallic phase occurred all throughout the surface, with globular formation in case of reduction where hydrogen was the carrier gas.