THE PRODUCTION OF STEEL POWDERS BY HYDROGEN REDUCTION OF IRON AND ALLOYING METAL CHLORIDES.

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Keywords: Thermodynamics, Reduction.

Compounds: Iron, Nickel, Chromium and Cobalt Powders.

ABSTRACT

The reduction of molten metal chlorides at temperatures below the melting point of the metal offers the possibility of producing fine metal powders at a lower energy cost than existing processes. Equilibrium composition of iron, nickel, chromium, and cobalt chlorides with hydrogen presented here, indicate the feasibility of the proposed process, as do initial experimental measurements.

1. INTRODUCTION

In the present route to steel, ores are beneficiated to about 93% oxide and fed to a blast furnace where 2 tonnes of iron are produced for approximately 1 tonne of coke. This represents about 50% more than the theoretical thermodynamic minimum(1). The use of hydrogen reduction of iron chloride, produced by leaching the ore, or dissolving scrap, with hydrochloric acid followed by drying and melting, could be employed at either low or high temperature to yield either a pure iron powder or a pure iron melt.

The first step in the process is to treat iron ore with hydrochloric acid in the proportions necessary to give a ferric chloride liquor.

$$Fe_2O_3 + 6HCl \rightarrow 3H_2O + 2FeCl_3$$

The ferric chloride is filtered from the gangue and passes through an evaporator/crystalliser in which partial reduction to ferrous chloride is achieved by hydrogen.

$$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$$

Ferrous chloride is then passed to a melting stage where chlorides of alloying metals may be added, and then sprayed into a reaction chamber where it meets a flow of hydrogen at about 1200K. In this chamber, the chlorides are reduced to the metals. It is intended that the droplets should be finally reduced to small metal spheres composed of micro-particles of the individual pure metals, provided a certain amount of sintering occurs during the reduction process. The reaction can be described by

$$FeCl_2 + H_2 \rightarrow Fe + 2HCl$$

for ferrous chloride reduction, with similar reactions for the other metal chlorides present.

The product is then collected as a bed of granules, themselves an intimate mixture of fine particles of the metallic constituents. These granules would then be subject to powder metallurgy techniques to produce mild steel or stainless steel strips for example.

Thus in this process the element chlorine is present either as hydrogen chloride or as a metal chloride; it circulates within the system and is not consumed.

2. METHOD OF CALCULATION

It can be shown that equilibrium in a chemically reactive system corresponds to a minimum in the Gibbs free energy of the system so that the sum of the chemical potential at equilibrium for the reactants equals that of the products(2). The chemical potential of a gas can be written as a function of its potential at standard conditions, the temperature and its partial pressure (or fugacity for non-ideal gases), and thermodynamic data is available in ideal gas form for most compounds (3, 4, 5). Using the relationship between the equilibrium constant of a reaction and the partial pressures of the constituents of the reaction, and together with the equation for overall molar balance, a set of simultaneous equations for the partial pressures of the gaseous species present can then be derived and solved. In the case of condensed species their chemical potential is independent of pressure and their mass fractions are calculated from the molar balance. This procedure is described in detail in Reference 6.

3. RESULTS OF CALCULATIONS AND DISCUSSION

3.1 Iron Chloride Reduction

When hydrogen and ferrous chloride are mixed in a molar ratio of unity the yield of iron is approximately 50% at 1200K. When M (moles H_2 : moles $FeCl_2$) is increased to eight, the percentage conversion of ferrous chloride to iron is increased to 95%, in addition to an increase in yield, the temperature at which the maximum yield occurs reduces from 1200K when M is unity to 900K.

At temperatures above 950K the reaction is endothermic: for example, to maintain 1100K at a molar ratio of two, 1.6 GJ/tonne of iron produced must be supplied. However, if the products are removed at temperatures below 950K then energy in excdss of that supplied can be abstracted. The energy required to achieve the reaction temperature can be supplied by the hydrogen.

The reaction equilibrium for a stoichiometric mixture of hydrogen and ferric chloride was computed and shows that ferric chloride does not exist in any measurable quantity in the presence of hydrogen at temperatures above 800K; it is completely reduced to ferrous chloride, the reduction of which proceeds as above.

3.2 Nickel Chloride Reduction

For a molar ratio of nickel chloride to hydrogen of unity, 100% reduction is effected at 1000K. Increasing the molar ratio of hydrogen broadens the mass fraction peak of nickel so that, at a molar ratio of eight to one, the 100% yield ranges from 800K to 2000K.

At 1100K 1.5 GJ of energy/tonne nickel is needed, independently of the molar ratio, to maintain the reaction temperature.

3.3 Chromous Chloride Reduction.

The results of the calculation of the reaction equilibrium for the chromous chloride/hydrogen system show that for a molar ratio of unity, the maximum yield is 24% which increases to 70% at a molar ratio of eight. This latter maximum yield occurs at 1280K, which is substantially higher than the equivalent temperature for ferrous chloride; to hold the products at this temperature, 7GJ of energy per tonne of chromium produced are required. This is a significant increase over that required for the equivalent ferrous chloride/hydrogen system.

3.4 Cobalt Chloride Reduction

For a molar ratio of cobalt chloride to hydrogen of unity, 92% reduction is effected at 1100K, with a molar ratio of two, 100% reduction occurs over a temperature range of 700-1100K, the enthalpy required in this latter case is 1.4 GJ/tonne cobalt.

3.5 Co-reduction of Chlorides

Simultaneous reduction of ferrous and chromous chloride in the ratio of 9 to 1 by hydrogen was investigated at a molar ratio of eight. Very little chromous chloride is reduced although over 90% of the ferrous chloride is reduced. At the temperature of maximum reduction of ferrous chloride, chromium exists almost entirely as the chloride. The implication of this result is that any scheme to produce a ferrochrome alloy using low molar ratios of hydrogen may have to involve separate reduction processes each at the optimum temperature for each alloying metal.

The results of the calculation of the co-reduction of ferrous, nickel and chromous chlorides in the ratio of the composition of an 18/8 stainless steel with a molar ratio of eight show that the yield of iron is in excess of 90%, the yield of nickel is 100% and the yield of chromium is negligible. The effect of increasing the molar ratio of hydrogen to 24 is to improve the iron yield to almost 100% and the chromium yield to 50%.

4. EXPERIMENTAL MEASUREMENTS

As mentioned in the introduction it is proposed to spray molten droplets of the chloride into an atmosphere of hydrogen. The thermodynamic data have shown the feasibility of the process but, of course, give no information about the reaction times involved. Measurements have been carried out using a thermogravimetric balance in which a molten sample of chloride was suspended in a furnace from one arm of a sensitive electronic balance while pure hydrogen was passed over it. Initially, approximately 10 mg of chloride were held in a platinum crucible and reduction effected at various temperatures throughout the range of interest. Measurements presented here indicate that, although the chlorides concerned have an appreciable vapour pressure at the desired reaction temperatures, once hydrogen is admitted to the sample there is no further vapour loss and all the product metal powder is formed within the crucible, indicating that the reaction occurs at the melt surface and not in the vapour phase. Although the reduction times are of the order of a minute, the sample used was considerably larger than that envisaged for droplet reduction ($\sim 100\,\mu g$). Further measurements with suspended droplets indicate reaction times of the order of seconds.

5. CONCLUSION

The reduction of iron and alloying metal chlorides with hydrogen to produce steel powders has been shown to be feasible from a theoretical standpoint. Measurements being carried out at present indicate the experimental feasibility of the process. Another paper at this conference shows that the process can save considerable energy compared to existing powder production practice.

6. REFERENCES

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