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THE KINETICS OF REDUCTION OF SYNTHETIC ULVOSPINEL IN A HYDROGEN ATMOSPHERE

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Ulvospinel, having the composition Fe_2TiO_4, was prepared by heating an intimate mixture of Fe_2O_3 and TiO_2 in a controlled atmosphere of CO_2 and H_2. The kinetics of its reduction by H_2 was studied. The parameters controlling the rate of reduction, such as temperature, granulometry and hydrogen partial pressure were investigated. The optimum temperature range for reduction of the ulvospinel to TiO_2 and Fe was established to be between 600° and 800°; above 800° reduction of the TiO_2 commenced.

The mineral ulvospinel, Fe_2TiO_4, occurs in nature namely in some ore deposits of Scandinavian countries [1]. Chemically, it is located in the ternary diagram, $FeO-Fe_2O_3-TiO_2$, which has been studied by several investigators [2—6]. In addition to the scientific interest, ulvospinel has a particular importance in metallurgical processes: it is an intermediary compound formed during the reduction of natural ilmenites. A knowledge of the kinetics of ulvospinel reduction is advantageous to explain the overall reduction of natural ilmenites which are an important source for TiO_2.

Several methods concerning the synthesis of ulvospinel from Fe_2O_3 and TiO_2, or from FeO and TiO_2, mixtures are known [6—10]. In the present work the product was obtained by heating a stoichiometric mixture of Fe_2O_3 and TiO_2 in a hydrogen atmosphere diluted with a controlled partial pressure of CO_2.

This method is suitable because the synthesis can be easily effected in a thermoanalyser where it is possible to control the operating conditions, and also to follow the different steps of the overall reaction.

The required stoichiometric mixture was prepared from Fe_2O_3 99.65% pure (the chief impurity was NH_4OH which is eliminated by heating) and anatase (TiO_2) 99.98% pure. Both compounds were finely ground and dried before mixing and compressing into miniature briquettes at 10,000 lbs/sq.in. The reducing atmosphere was obtained by mixing controlled flows of pure gases. Several test runs were made to arrive at the best CO_2/H_2 ratio and the best heating rate.

It was found that a pressure ratio (pCO_2/pH_2) of 0.85, and a heating rate from room temperature to 1300° of 25°/minute followed by cooling at 10°/minute, were suitable but not necessarily optimum conditions.

Five five-gram batches were prepared under the above described conditions with a holding period of one hour at 1300° before cooling.

The average weight loss was 99.1% of theoretical for the overall reaction:

$$Fe_2O_3 + TiO_2 + H_2 \rightarrow Fe_2TiO_4 + H_2O \qquad (1)$$

Debye – Sherrer patterns showed the product to be ulvospinel, no other structures being detected within the limits of precision of the method.

Reduction of ulvospinel

Constant parameters

The ulvospinel batches were ground as one lot. Screen analysis showed the following distribution:

+ 140 mesh	0.0%
140 × 325 mesh	39.4%
325 × 400 mesh	12.3%
– 400 mesh	48.3%

All reactions were run with this granulometry except when the influence of particle size was investigated.

The powder was introduced unpacked in a test-tube shaped platinum crucible (0.788 cm diam. × 2.03 cm length) which in turn was placed in the holder inside the Mettler thermoanalyser. All experimental conditions were kept constant as, for example, the sequence of heating in an argon atmosphere followed by its replacement by hydrogen:

– The air was evacuated from the furnace chamber containing the ulvospinel in the crucible, and the chamber was filled with argon at atmospheric pressure;

– The temperature was increased quickly, at a rate of 25°/minute, to reach the final temperature;

– The argon was withdrawn from the chamber and the hydrogen gas was quickly introduced until atmospheric pressure was reached. Then, a flow rate of hydrogen was kept constant at 20 liters per hour.

Preliminary experiments have shown that the initial rate of reduction is independent of the flow rate and pressure of hydrogen.

Variable parameters

The kinetics of ulvospinel reduction is affected by some factors which must be studied individually to obtain an acceptable mathematical expression for the reaction rate. These are:

the temperature of isothermal reduction;
the granulometry of the powder;
the mass of the ulvospinel.

Preliminary tests

Three tests were run on 50.0 mg of ulvospinel powder at one atmosphere pressure. The flow rate of hydrogen was 13 l/h and heating rates from room temperature to 1250° were respectively 10°, 15° and 25°/minute for the 1st, 2nd and 3rd tests.

The results are shown in Fig. 1.

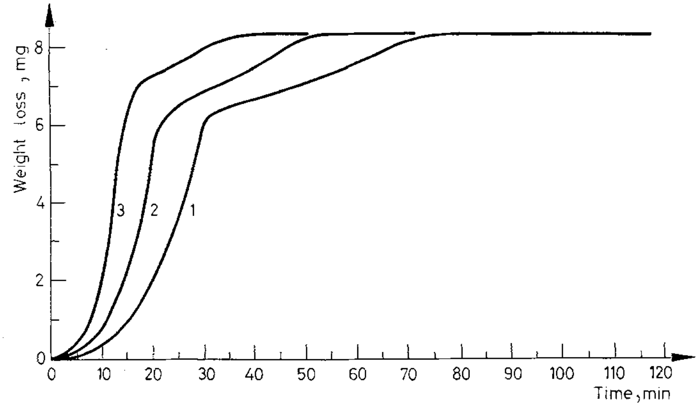

Fig. 1. Preliminary tests. The initial temperature is 500° and heating rates are respectively 10, 15 and 25°/min for the curves 1, 2 and 3

The two inflections for each curve indicate that the reduction process is a two-step reaction corresponding to the reactions (2) and (3), iron being preferentially reduced at lower temperatures, after which the second and more difficult reaction takes place at approximately 800° at a much slower rate than the first.

$$Fe_2TiO_4 + 2\,H_2 \rightarrow 2\,Fe + TiO_2 + 2\,H_2O \qquad (2)$$

$$TiO_2 + 1/3\,H_2 \rightarrow 1/3\,Ti_3O_5 + 1/3\,H_2O \qquad (3)$$

For an initial weight of 50.0 mg of ulvospinel, the theoretical weight loss of oxygen for the reactions (2) and (3) are respectively 7.14 mg and 1.26 mg. These values were found in one experimental run with a 25°/minute heating rate. It is to be noted that the total weight loss of 8.33 mg was constant, independent of the heating rate, and was in agreement to within 1% with the total theoretical weight loss of 8.40 mg.

Experimental results

The effect of temperature

Fig. 2 shows results obtained by measuring isothermal reduction at nine different temperatures.

The global reaction of the reduction may be written as follows:

$$Fe_2TiO_4 + (4 - n)\, H_2 \rightarrow 2\, Fe + TiO_n + (4 - n)\, H_2O \qquad (4)$$

Then, the numerical value of n can be calculated from the measured weight loss, w.

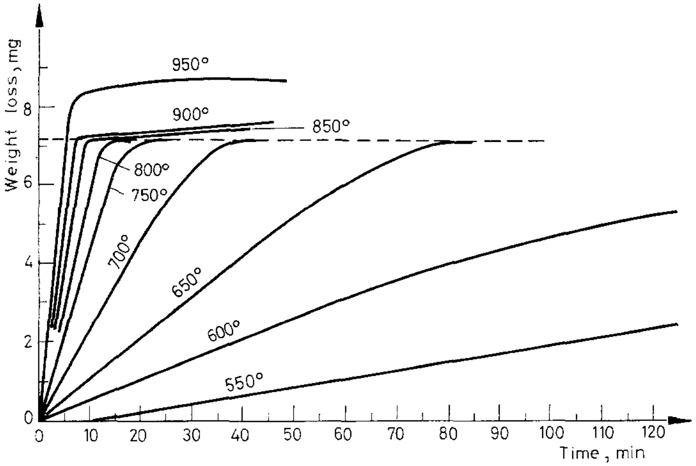

Fig. 2. Isothermal reduction of ulvospinel at nine temperatures in a hydrogen flow rate of 20 l/h at atmospheric pressure on 50.0 mg sample

For an initial weight of 50 mg of ulvospinel it can be shown that, when the value of n is 2, the theoretical weight loss is 7.14 mg. Consequently, according to the reaction (4), the weight loss is given by:

$$w = 14.28 - 3.57\, n$$

from which n is given by:

$$n = (14.28 - w)/3.57 \qquad (5)$$

Under 800° the weight loss is 7.14 mg and the value of n is 2, so the reaction of the reduction is given by Eq. (2).

The products of the reaction, Fe and TiO_2, were identified by X-ray analysis.

Above 800° the reduction of TiO_2 started but it was very slow.

At 900° and 950° the total weight loss did not correspond to theoretical weight loss (8.40 mg) for the reaction

$$Fe_2TiO_4 + 7/3\, H_2 \rightarrow 2\, Fe + 1/3\, Ti_3O_5 + 7/3\, H_2O \qquad (6)$$

At 950°, the weight loss gives a value of n equal to 1.56 instead the theoretical value of 1.66 for the above reaction. The reduction may have gone a step further than Ti_3O_5, for example to Ti_2O_3, in a very modest way. This is difficult to prove by X-ray diffraction methods since it is quite impossible to detect small quantities of Ti_2O_3 in a mixture of Fe and Ti_2O_5.

The effect of granulometry

From the results reported in Fig. 3, it follows that the reaction rate decreases with increasing particle size. Isothermal reductions were run at 650° on three 50.0 mg sample of ulvospinel at a hydrogen flow rate of 20 l/h and at atmospheric pressure. In the three tests the average diameters of ulvospinel particles were respectively 0.046, 0.158 and 0.358 mm.

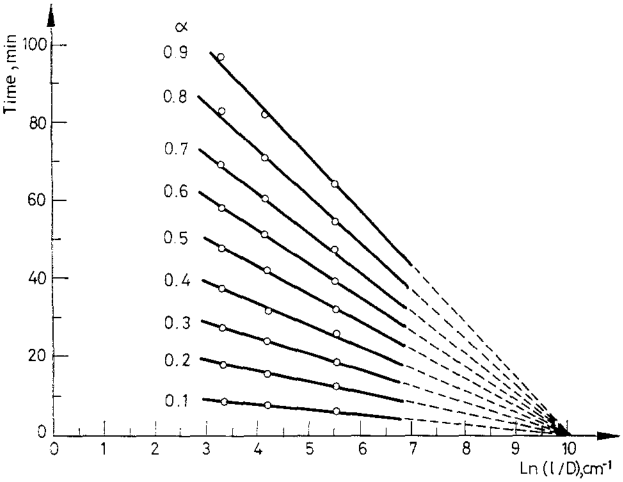

Fig. 3. Influence of particle diameter of ulvospinel powder on the time of reduction. α: fraction of ulvospinel reduced

In the same figure the reaction time is plotted versus ln $(1/D)$, where D is the diameter of the particles. For each degree of reduction (α) the three points obtained lie on perfect straight lines which converge to a value of D equal to $4.24 \cdot 10^{-5}$ cm. At this value of D the reaction should be instantaneous.

The effect of ulvospinel mass

The effect of mass was determined in four reduction tests on different thicknesses of ulvospinel. The other operating conditions were kept constant, namely a hydrogen flow rate of 20 l/h at one atmosphere pressure, and isothermal conditions at 650°.

The results reported in Fig. 4 show that the reaction rate decreases when the ulvospinel mass increases.

It is possible to calculate (e) the maximum thickness of the powder in the platinum crucible since its bottom is a portion of a sphere with a radius (R). If the spherical portion occupied by the powder has a surface of radius r, its volume (V) may be given:

$$V = \frac{\pi e^2}{3}(3R - e) \tag{7}$$

It may be shown that there is a simple relation between (R), (r) and (e):

$$R^2 = r^2 + (R - e)^2 \tag{8}$$

The inside diameter ($2R$) of the platinum crucible was measured as 0.788 cm and the specific mass of the powder was determined as 1.94 g/cm^3. By combining equations (7) and (8) the maximum thickness (e) of the powder can be determined:

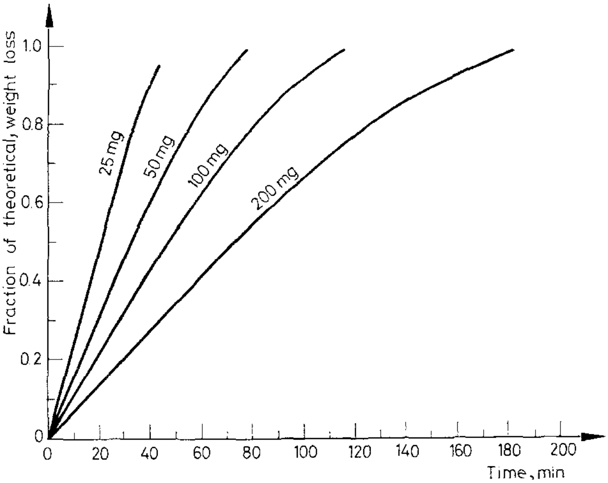

Fig. 4. Isothermal reduction of different masses of ulvospinel at 650° in a hydrogen flow rate of 20 l/h at atmospheric pressure

$$e = 3\left(R - \frac{V}{\pi e^2}\right) \tag{9}$$

If the mean thickness (e_m) of the powder is defined as being equal to $V/\pi r^2$, the rate of reaction may be studied in relation with this parameter. The values of (e) and (e_m) for different masses of ulvospinel powder have been calculated and are reported in Table 1.

Table 1

Effect of mass of ulvospinel

Mass of sample, mg	Maximum thickness of powder, cm	Mean thickness of powder, cm
25	0.107	0.0563
50	0.155	0.0836
100	0.227	0.1288
200	0.342	0.2151

Fig. 5 shows the fitting of the maximum thickness (*e*) versus the time of reaction. Such a fitting gives a straight line. A test made with 100 mg of ulvospinel in the same experimental conditions but using a crucible with a diameter of 1.60 cm shows that the reaction rate is independent of the diameter of the crucible.

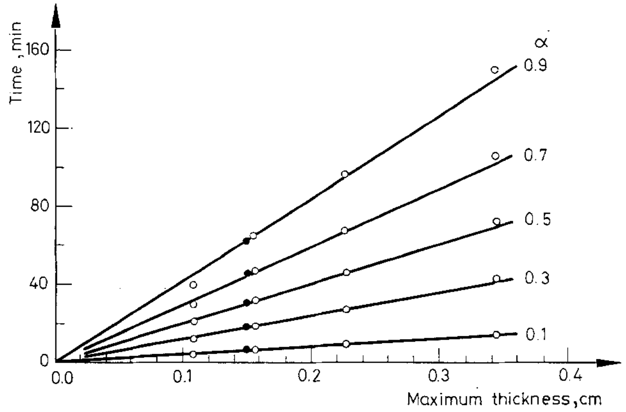

Fig. 5. Influence of the maximum thickness of ulvospinel powder on the rate of reduction. α is the fraction of ulvospinel reduced. ○ indicates the test with a crucible having a diameter of 1.60 cm

Reproducibility test

To verify the reproducibility of the results obtained, three experiments of isothermal reduction were run on 50 mg of ulvospinel at 650° in a hydrogen flow rate of 12.3 liters/hour.

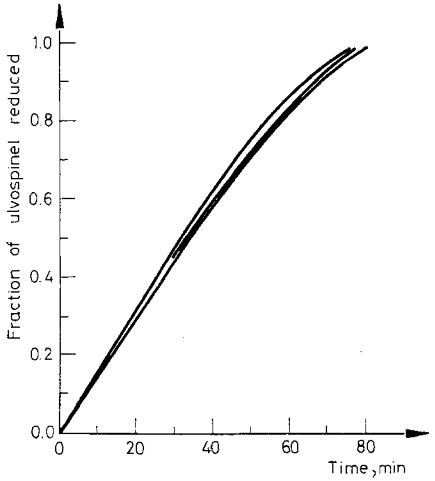

Fig. 6. Reproducibility test

The results are shown in Fig. 6. The time of reaction was precise to 3% and the weight loss was found reproducible with a relative error of 0.85% of theoretical.

Discussion and conclusion

Under the described experimental conditions several factors can control the reaction rate:

1. Diffusion of gas through the surface of the powder;
2. Diffusion of gas between the particles;
3. Diffusion of gas inside the particles;
4. Progress of the reaction interface.

The reaction rate being independent of the hydrogen flow rate, the first mechanism does not influence the reaction.

Table 2 summarizes the influence of different parameters on each forementioned mechanism which control reaction (2).

Table 2

Influence of different parameters on the reduction of ulvospinel by hydrogen

Mechanism	Influence on the reaction rate with an increase of			Influence on the initial reaction rate with an increase of particle size
	hydrogen flow rate	particle size	thickness of ulvospinel	
Diffusion between the particles	constant	increase	decrease	increase
Diffusion inside the particles	constant	decrease	constant	constant
Progress of the reaction interface	constant	decrease	constant	decrease
Experimental results	constant	decrease	decrease	decrease

The progress of the reaction interface is more important than the diffusion between the particles of the powder, because the rate of reaction decreases with an increasing particle size of ulvospinel powder.

The kinetic equation of the progress of the reaction interface for the reduction of large size spherical particles may be given by the following equation:

$$\frac{1-(1-x)^{1/3}}{t} = k \exp\,(-E_a/RT)/D \qquad (10)$$

where x is a fraction of initial mass of ulvospinel reduced and D the diameter of the particles of the powder. This equation is often used to study the kinetics of reduction of iron oxides.

In this investigation since the granulometry was very small and the porosity very large, the specific surface at the reactive interface remained quite constant. Consequently the degree of reduction (x) is a linear function of time. For the same reason the reaction rate does not vary with $1/D$ but it is a function of $\ln(1/D)$. The surface of reactive interface decreases appreciably only at the end of the reaction.

Therefore Eq. (10) becomes

$$\frac{x}{t} = k\, k_t \ln(1/D) \tag{11}$$

where k_t is a constant depending only on temperature and equal to $\exp(-E_a/RT)$. When the progress of the reaction interface is a controlling factor, the reaction rate is influenced by the pressure of reducing gas.

As the tests were run on powder, the diffusion of water produced and the reactivity of particles generate a gradient of pressure in the hydrogen. At the surface of the powder the particles react rapidly because the partial pressure of hydrogen is greatest at that point. But the observed rate is an average one.

The study of the influence of hydrogen pressure (p) at the surface of powder, and the average thickness of the powder, permit to calculate the value of k as a function of those two parameters

$$k = k_r\, p^{0.37}/e_m \tag{12}$$

where k_r is a constant independent of temperature, hydrogen pressure, granulometry and the average thickness of the powder.

Eq. (11) is substituted in Eq. (12) to obtain

$$\frac{x}{t} = k_r\, p^{0.37}\, k_t \ln(1/D)/e_m \tag{13}$$

where t is time in minutes, p pressure in mm of mercury, D the diameter of particles of powder in cm, and e_m the average thickness of the powder in cm. The constant k_r is independent of all experimental parameters and k_t is a constant which is a function of temperature only, and equal to $\exp(-E_a/RT)$. The experimental values for k_r and E_a are respectively 1.24 and 20 200 cal/mol. Eq. (13) can be applied for temperatures ranging from 600° to 850°.

Due to the small size of the crucible it was impossible to determine the relation between the partial pressure of hydrogen through the powder and the hydrogen pressure at the surface of the powder. For this reason the influence of diffusion is considered as a function of e_m.

The value of activation energy for the reduction of Fe_2TiO_4 to $2Fe + TiO_2$ by hydrogen is 20.2 kcal/mol. Yamaguchi and his coworkers [11] found an activation energy of 21 kcal/mol for the reduction of Fe_2TiO_5 to 2Fe + TiO_2 by hydrogen. Feinman and Drexler [12] reported a value of 16.4 kcal/mol for the reduction of FeO by hydrogen. Imoto and Moriyana [1] obtained a value of 17.7 kcal/mol for the reduction of Fe_2O_3.

The difference between the values found for the two titanium compounds is quite similar to that between the values reported for the two iron oxides, which seems to reflect the state of oxidation of iron in the two titanium compounds.

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Résumé — On a préparé l'ulvospinelle de composition Fe_2TiO_4 en chauffant un mélange de Fe_2O_3 et TiO_2 dans une atmosphère contrôlée de CO_2 et H_2. On a étudié la cinétique de sa réduction par H_2. On a suivi l'influence des paramètres qui déterminent la vitesse de la réduction, tels que la température, la granulométrie et la pression partielle d'hydrogène. On a trouvé que le domaine de température le plus favorable à la réduction de l'ulvospinelle en TiO_2 et Fe se situait entre 600 et 800°; la réduction de TiO_2 commence au-dessus de 800°.

Zusammenfassung — Ulvospinell der Zusammensetzung Fe_2TiO_4 wurde durch Erhitzen einer innigen Mischung von Fe_2O_3 mit TiO_2 in einer geregelten Atmosphäre von CO_2 und H_2 hergestellt. Die Kinetik der Reduktion desselben durch H_2 wurde studiert. Die Parameter, welche die Reduktionsgeschwindigkeit bestimmen, wie Temperatur, Korngröße und Partialdruck des Stickstoffs wurden geprüft. Der optimale Temperaturbereich für die Reduktion von Ulvospinell zu TiO_2 und Fe war zwischen 600° und 800°; über 800° begann die Reduktion von TiO_2.

Резюме — Ульвошпинель состава Fe_2TiO_4 приготовлен нагреванием однородной смеси Fe_2O_3 в контролируемой атмосфере CO_2 и H_2. Изучена кинетика его восстановления водородом. Исследованы параметры, контролирующие скорость восстановления, такие как температура, гранулометрия и парциальное давление водорода. Установлено, что оптимальная область температур для восстановления ульвошинеля до TiO_2 и Fe находится между 600°—800°; выше 800° начинается восстановление TiO_2.