KINETICS AND MECHANISM OF ZINC FERRITE FORMATION

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(Received 20 July 1979)

ABSTRACT

The kinetics and mechanism of zinc ferrite formation are studied for pure oxide mixtures at temperatures up to 1000°C by X-ray analysis, DTA and chemical analysis. Formation of ferrite obeys a random nucleation equation with an activation energy of 29.4 kcal mole^{-1} in the temperature range 635—780°C. The nucleation process is followed by formation of spinel in an ordered lattice at temperatures >800°C. The possibility of ZnO dissolution in the ferrite is also considered for ZnO at ratios higher than equimolecular.

INTRODUCTION

It is well known that under certain roasting conditions for zinc sulphide ores, zinc and iron oxides combine to form zinc ferrite. The formation of this ferrite is dependent both on iron content and roasting temperature. This reaction is of considerable importance in the extraction of zinc by the acid leaching of roasted sulphides.

Extensive studies have been done on zinc ferrite preparation under different sintering conditions. It was found that the greater the contact between iron and zinc oxides and the higher the sintering temperature, the greater is the amount of ferrite formed. Some authors [1—3] prepared zinc ferrite at temperatures between 600°C and 800°C; others [4—6] considered that temperatures as high as 1300°C were most favourable. Toropov and Borisenko [4] found that the sintering of pressed samples of ZnO and Fe$_2$O$_3$ at 1100°C needed 19 h for complete reaction. Rigden [7] found that sintering of the oxides at temperatures >1300°C could not be recommended because of the volatility of ZnO.

The mechanism of zinc ferrite formation has been considered only by a few authors [8—11]. Hopkins [8] assumed that the reaction is controlled by diffusion of iron(III) oxide through the ferrite layers, while Duncan and Stewart [11] considered it is controlled by diffusion of the more mobile ZnO into the ferrite already formed. In addition, there are great discrepancies in the quoted values for the activation energy of zinc ferrite formation, ranging from 14.0 kcal mole^{-1} [12] to 110 kcal mole^{-1} [8].

The contradictory data given in the literature show the need for further study on the mechanism of formation of zinc ferrite. We have used DTA and X-ray diffraction studies to investigate temperature effects and the kinetics of formation.

EXPERIMENTAL

Materials

The materials used were chemically pure. Zinc oxide was heated at 500°C to decompose any zinc carbonate present. Iron(III) oxide was prepared from pure iron(III) sulphate by precipitation, drying and ignition at about 800°C.

Apparatus and technique

A stoichiometric mixture of ZnO and Fe_2O_3 was mixed thoroughly in an agate mortar to reduce the particle size to —63 μm and attain a uniform mixture. Pressed samples of uniform density were prepared at a pressure of 40 kg cm^{-2} in a steel mould. These samples were heated in an oxygen atmosphere in an automatically regulated tubular furnace. The sintered samples were cooled according to the recommendations of Muan [13], crushed and pulverised to —74 μm. The products formed were subjected to chemical and X-ray analyses. Chemical analysis of unreacted zince oxide was done by leaching the sintered samples with sulphuric acid (0.5 M) at room temperature for 60 min and determining the zinc in the liquor. X-ray diffraction analysis was done with a Philips diffractometer type PW 1010, with Fe-filtered Co K_α radiation, and patterns were matched with ASTM cards.

The temperature range within which ferrite was formed was determined by DTA, with a sensitive apparatus of high resolution, locally made, and applying a special technique: 50-mg samples of the Fe_2O_3—ZnO mixture were pressed into a cup-shaped mould to obtain U-shaped blocks which were then placed tightly surrounding the differential thermocouple. The mechanism of ferrite formation was deduced from calculations of activation energies, derived from the results of DTA and with the aid of modified methods recommended by previous workers [14—16].

RESULTS AND DISCUSSION

Chemical analysis

Results of the analysis of mixtures sintered at different temperatures (600—1000°C) showed that samples prepared at 600°C contained 20% of unreacted zinc oxide, even after sintering for 300 min. However the amounts of free ZnO are minimal (5% and 2%) when sintering is carried out at 700°C and 800°C, respectively. Unreacted ZnO is almost negligible at higher sintering temperatures.

X-ray analysis

From the X-ray patterns given in Fig. 1 it can be seen that at 600°C both α-Fe_2O_3 and $ZnFe_2O_4$ are identifiable. Patterns of α-Fe_2O_3 are of higher intensity than those of $ZnFe_2O_4$ owing to the better crystallinity of α-Fe_2O_3. At 700°C and 800°C, α-Fe_2O_3 cannot be identified, which may be attributed to dissolution of free Fe_2O_3 in the ferrite lattice. Moreover, the X-ray lines for ferrite sintered at 600—800°C are broad, indicating that the ferrite prepared in this temperature range has a disordered lattice. This is further discussed below under DTA studies.
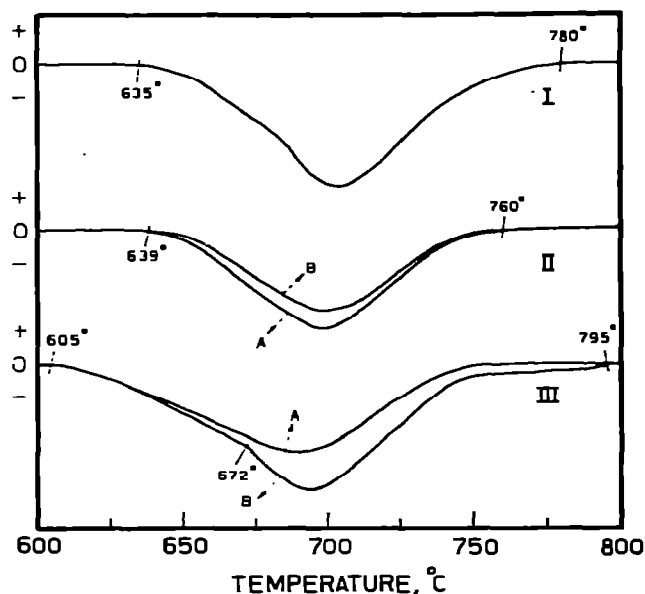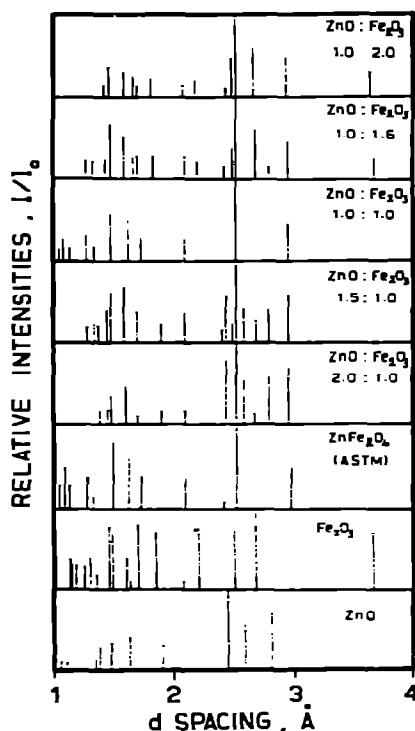
Fig. 1. X-ray Debyograms of the materials used and the zinc ferrite products prepared at different molecular ratios; sintering was at 900°C.

Fig. 2. DTA curves of Fe_2O_3 : ZnO mixtures of molecular ratios (I) 1.0 : 1.0; (II) (A) 1.4 : 1.0 and (B) 1.8 : 1.0; (III) (A) 1.0 : 1.4 and (B) 1.0 : 1.8.

Loss in weight

It is noteworthy that zinc ferrite formation at temperatures >700°C is accompanied by a slight loss in weight (ca. 0.1%). This effect is independent of time or temperature of sintering and may be attributed to the removal of small amounts of oxygen, as mentioned by Rigden [7].

DTA studies

The above-mentioned results seem to contradict other work given in the literature which indicates that zinc ferrite must be prepared at relatively high temperatures. In order to throw more light on the method and temperature required for zinc ferrite preparation, a DTA experiment was done on an equimolecular mixture of ZnO and Fe_2O_3 pressed into cup-form and placed over the differential thermocouple. The results, given in Fig. 2, show that ferrite formation is characterised by a broad endothermic peak starting at 635°C and ending at 780°C. This broadness indicates that ferrite formation proceeds at a relatively slow rate in the temperature range 635—780°C.

It is interesting to note the change in the DTA peak brought about by change of the molecular ratio ZnO : Fe_2O_3, as illustrated in Fig. 2. The reaction starts at lower temperatures (605°C) for high ratios of ZnO : Fe_2O_3, but is complete at the same temperature as that shown for the equimolecular ratio. Moreover, for mixtures containing a ZnO : Fe_2O_3 ratio of 1.8 : 1.0, a

kink is observed in the DTA peak at 672°C in addition to the shoulder which extends from 755°C to 795°C. This phenomenon is not observed for mixtures containing lower amounts of ZnO. However, for mixtures of Fe_2O_3 : ZnO ratio >1 : 1, the DTA curves obtained do not show any deviation from that of the equimolecular ratio.

Mechanism of ferrite formation

In order to investigate the mechanism of the process, both the rate-controlling reaction and the activation energy must be determined. In many cases the actual kinetic equations are rather complicated and the methods considered by some authors [7,8,11] cannot be applied without modification in the wide temperature range used in the process. The most recent method of obtaining thermogravimetric curves [15—17], with the help of previous investigations [18,19], can be applied sucessfully in the present work. However in this study the DTA curves are analysed by a new process derived to suit Šatava's calculations [16], according to the following steps.

(i) The area surrounded by the DTA curve on one side and the base line on the other, which represents the heat (enthalpy) taken up by the reactants, is measured by a planimeter and considered to correspond to a reaction extent of unity. This area is further divided by drawing parallel lines perpendicular to the temperature axis to form a number of small areas, each representing different fractions of the extent of reaction with respect to temperature range. The reacted fraction (α) is calculated for each small area. On plotting α against the appropriate absolute temperature, the curve illustrated in Fig. 3 is obtained, which is similar to that for conventional TGA.

(ii) By applying the various kinetic equations of Sharp et al. [14] (listed in Table 1) and using the recommended procedure of Šatava [17] for thermogravimetric results, curves for the reactions assumed to represent the most probable kinetic equation are easily plotted, as shown in Fig. 4. The correct kinetic equation is that giving a straight line in the log $g(\alpha)$ vs. $1/T$ plot.

The function A_3 given by Avrami for a random nucleation reaction, is the most appropriate, giving a straight line of slope -4.6×10^3 d log $g(\alpha)$/d $1/T$:

$$A_3 : [-\ln(1 - \alpha)]^{1/3} = kt$$

Accordingly, the activation energy for zinc ferrite formation in the temperature range 642—768°C is 29.4 kcal mole^{-1} from the calculations given by Šatava [17]. The small deviations from linearity which arise on plotting the function A_3 may be related to interfering reactions; more complicated equations are necessary to describe these effects. The method of calculation used here is much easier and more accurate than other methods [18—20].

The value of activation energy deduced from the present study is markedly lower than that given by previous authors [7—11]. This disagreement is attributed both to the methods applied for calculation of activation energy and the different ranges of temperature used. Most studies have taken place at relatively high temperatures. Kushima et al. [9,10], working in a narrow range of temperature (750—800°C) and using a different technique for rate measurement, determined an activation energy of 63 kcal mole^{-1}. In
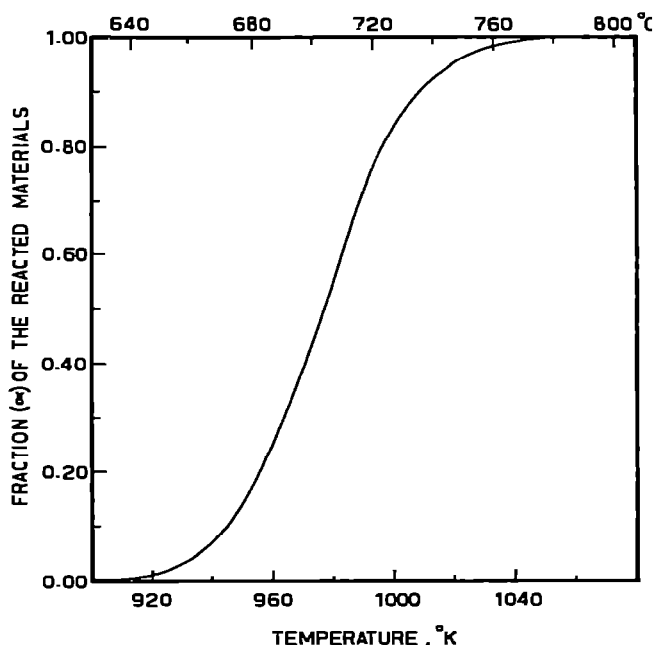
Fig. 3. Relationship between the fraction (α) of reacted materials and the temperature of zinc ferrite formation.

the present work it was found that more than 90% of the zinc ferrite was formed at temperatures lower than 750°C, and reaction was complete at 780°C. It is interesting to note that Kleinert [21] found that spinel formation begins for all ferrites at 663°C, and for zinc ferrite occurs in the temperature range 650—700°C [22].

TABLE 1

Kinetic equations applied to solid-state reactions

| Function	Equation	Rate-controlling process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D_4	$(1-2/3\alpha)-(1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling—Brounshtein equation
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle
A_2	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation; Avrami equation I
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation; Avrami equation II
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry
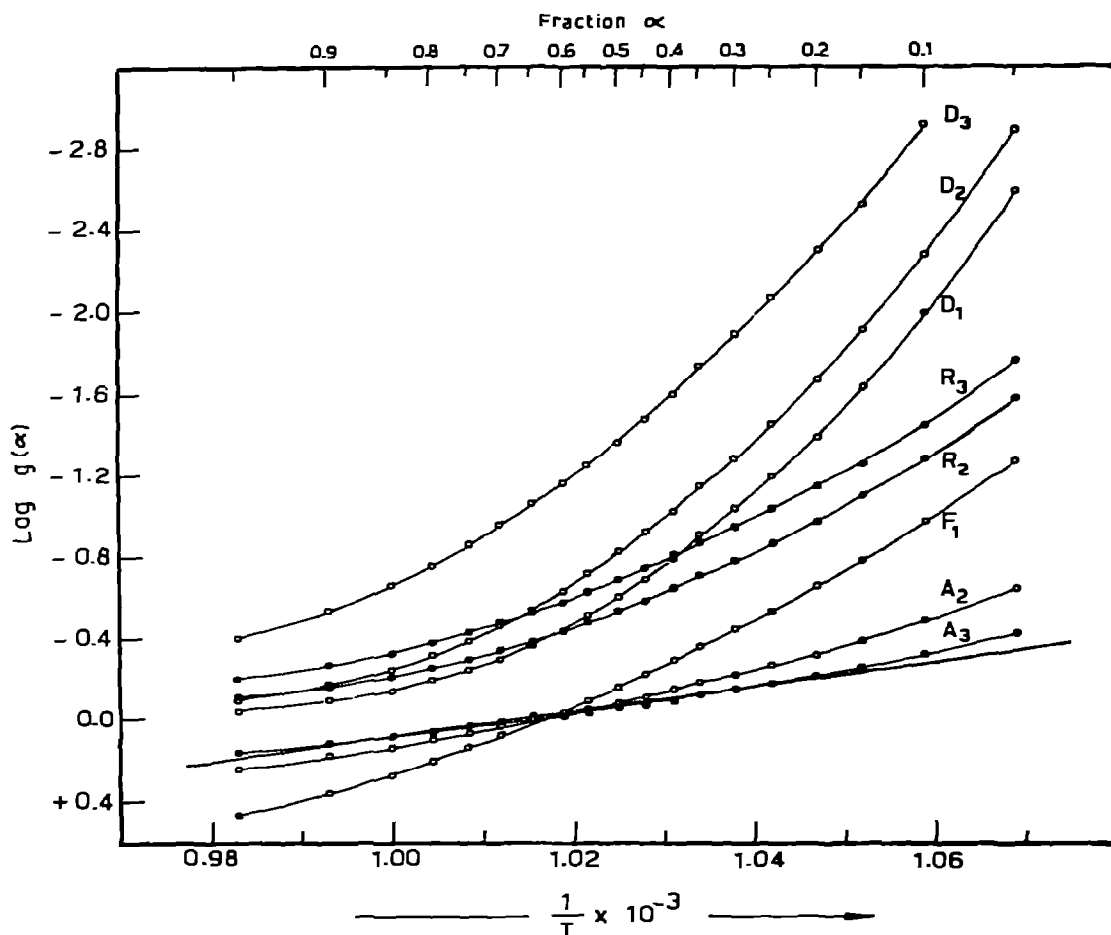
Fig. 4. Plot of log $g(\alpha)$ versus $1/T$ for the formation of zinc ferrite, applying the various functions of a solid-state reaction.

CONCLUSION

The solid-state reaction between ZnO and Fe_2O_3 undergoes the following steps.

(i) The reaction between ZnO and Fe_2O_3 starts at $642°C$ and proceeds at a random nucleation rate in the temperature range $635—780°C$.

(ii) The zinc ferrite nuclei formed do not acquire a well defined spinel structure before $800°C$, as shown by the broad lines of the X-ray diffraction analysis. The ferrite formed exists in a disordered lattice, even after heating the compound for 300 min. This disordered lattice is a transition structure, partially leached by sulphuric acid (0.5 M), and behaves differently from ferrites sintered at temperatures $>800°C$. Accordingly, one can expect that bonding of cations in an ordered manner only exists at relatively high sintering temperatures, proceeding via the disordered lattice through a number of solid solutions. The formation of spinel ferrite with a definite structure necessitates both high temperatures ($>800°$) and long reaction periods.

This conclusion explains the discrepancy between the results of DTA, chemical analysis and X-ray analysis for ferrites formed at different temperatures. It also explains the great differences between the calculated values of activation energy based on the results of DTA (29.4 kcal mole^{-1}) and those determined with different techniques (14 [12], 43 [22], 57 [8], 63 [10], 95.5 [11] and 110 [8] kcal mole^{-1}). The high values reported by most of these authors, based on the diffusion rates, occur because diffusion is taking place at relatively high temperatures through the initially formed layers of the spinel phase.

(iii) Spinel formation occurring at relatively high temperatures can be considered as a separate reaction which proceeds at a different rate and a different activation energy from that considered in (i) and (ii). When a DTA experiment was performed at a low rate of heating (2.5°C min^{-1}), another broad endothermic peak was displayed about 1000°C. This peak may be considered to correspond to the final spinel formation. Accordingly, preparation of zinc ferrite at relatively high temperatures (>1000°C) may proceed via transition steps which occur by spontaneous reaction at these high temperatures. The rate-determining step is spinel formation which proceeds via rearrangement of the ions in the compound formed. This also explains the activation energy values obtained by previous authors, which reach 95.5 kcal mole^{-1} for reactions proceeding at 1100—1300°C [11].

(iv) The presence of ZnO in ratios higher than stoichiometric accelerates the process of nucleation which occurs during the formation of ferrite (the transition step). The results of DTA of such mixtures show that the nucleation process starts at a relatively low temperature, 40°C less than that achieved at the equimolecular ratio. In addition, partial dissolution of ZnO in the ferrite, assumed by Kushima and Amanuma [10], explains the kink in the DTA curve at 672°C as well as the shoulder noted at 755—795°C for mixtures with a ZnO : Fe$_2$O$_3$ ratio of 1.8 : 1.0. This phenomenon was not noted with Fe$_2$O$_3$ in ratios higher than stoichiometric.

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