

Grain Growth in Barium Ferrite

I. Kinetics of the Formation of Barium Ferrite

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바리움페라이트내의 입자성장

제 1 보 바리움페라이트의 합성반응

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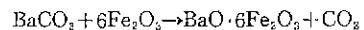
개 요

본 연구는 열분해반응(熱分解反應)에 의한 바리움 페라이트 합성반응($\text{BaCO}_3 + 6\text{Fe}_2\text{O}_3 \rightarrow \text{BaO} \cdot 6\text{Fe}_2\text{O}_3 + \text{CO}_2$) 후기(後期)에 있어서의 반응기구(反應機構)를 규명코자 수행되었다. 실험은 등온하(等溫下)에 900°C 부터 1100°C 까지 50 도의 간격으로 시행되었으며, 반응량(反應量)의 결정은 X-선(線) 회절분석법(廻折分析法)을 이용하여 기초실험에서 얻은 표준보정자료(標準補正資料)와 비교함으로써 이루어졌다. 연구실험결과 합성반응의 후기는 주로 확산기구(擴散機構)에 의해 지배되며 실험적으로 구한 활성화에너지(活性化 Energy)는 $14 \pm 10 \text{Kcal/mole}$ 이었다. 그리고 반응초기(反應初期)는 표면반응(表面反應)이나 혹은 반응후기와는 다른 이온(ion)에 의한 확산에 의해 지배될 것이다.

I. INTRODUCTION

Solid state reactions in ferrite formation have been the subject of much research, since the discovery of ferrite as a magnetic material by workers in Philips Laboratory⁽¹⁾ After World War II, much progress has been made, but there are many problems left to be explored concerning behavior of reactions in some ferrites. Rare data are available on the kinetics of the formation in barium ferrite and this work was initiated to give a quantitative interpretation of the kinetics.

In the present work we studied the kinetic-process occurring during a typical thermal decomposition reaction;



In the reaction between barium carbonate and ferric oxide, Ward and Struthers⁽²⁾ studied in the range from 610° to 970°C for equimolar mixture $\text{BaCO}_3 - \text{Fe}_2\text{O}_3$ by weighing carbon dioxide liberated. They obtained two activation energies, 25Kcal/mole and 19 Kcal/mole respectively associated with two products $\text{Ba}(\text{FeO}_2)_2$ and $\text{Ba}_2\text{Fe}_2\text{O}_7$. However, it is not clear whether this corresponds to the activation energy of

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formation of the reaction product or to that of decomposition of barium carbonate, since there is no reason to believe that latter process is rate-determining one.

In an oxide-oxide reaction of nickel ferrite Economos and Cleveger, Jr. (3), in reviewing the formation-kinetics, found that Jander's expression

$$(1 - \sqrt{1 - X})^2 = Kt$$

was not applicable either in the early stages of reaction or after the reaction had progressed for some-time. Where X is the fraction reacted, t the time, and K a reaction rate constant. They mentioned that a more detailed model would be desirable. However, an average of 56 Kcal was obtained for the activation energy. After that time Turnbull (4) reported that the reaction follows Tamman's law

$$C = A \log t + B$$

in nickel ferrite and magnesium ferrite. Where C is the fraction of formed at time t for a given temperature, and A and B are constants. In their study they found that a plot of concentration versus the logarithm of time gave two distinct slopes, which are related to the change in the diffusion mechanism with time. They interpreted that surface diffusion was significant in the 600° to 700°C range, and a gradual change-over to bulk diffusion took place as the reaction temperature went up. In their work activation energies for the surface diffusion and bulk diffusion are 30 Kcal and 18 Kcal and they suggest that the reaction mechanism was iron diffusing into an active metastable nickel oxide phase, although they could not elaborate what the metastable or active phase should be. Subsequently, Blum and Li (5) in the study of kinetics of nickel ferrite formation, criticized the Jander equation and gave a new expression

$$\frac{dx}{dt} = \frac{(a-x)}{t}$$

where x is the percentage of ferrite formed, t the time, and a the kinetic isothermal reaction rate coefficient.

From these short review it can be easily expected that the mechanism of the formation of barium ferrite may be due to a diffusion process. We will observe

the kinetics which occurs in the latter stages of the reaction to investigate the mechanism of the formation of barium ferrite under isothermal heat-treatment.

II. EXPERIMENTAL

A. Preparation of Samples

Reagent-grade barium carbonate and high-purity commercial ferric oxide were used as starting materials for the reaction. The purity of barium carbonate was 99.3% and a disturbing impurity was sulfate, 0.04%. Ferric oxide of 99.3 to 99.6% purity had impurities such as SiO_2 , TiO_2 , Al_2O_3 within 0.45%. The particle shape of ferric oxide powder was spherical and the predominant particle size was 0.3 to 0.8 μ . These two constituents were dried at 110°C for an hour to remove adsorbed moisture. They were then placed in a desiccator until they were cooled to room temperature. After cooling, the proper amount of barium carbonate and ferric oxide to give barium ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) after reaction was wet-milled in a still ball mill for 4 hours with distilled water. The resulting slurry was dried at 110°C and ground in a mortar. This homogenized mixture was stored in a desiccator before calcining.

Reaction was carried out at 50°C intervals in the temperature range 900° to 1100°C for various time at each temperature, in air atmosphere, under isothermal condition. The reaction temperature were selected according to References (6) (7). Each time, 30 grams of powdered sample was loosely compacted in a reaction vessel used and placed in a muffle box furnace maintained at the given constant temperature. After the pre-determined time the sample was air quenched by removing it from the furnace, reground in a mortar below 200 mesh, and placed again in a desiccator before an X-ray analysis.

Precise corrections to the temperature readings were made by a Pt/Pt-Rh 13 thermocouple in contact with the reaction vessel and the temperature fluctuation in heating zone was $\pm 3^\circ\text{C}$, which were measured by another thermocouple.

B. X-Ray Analysis

A Shimadzu GX-3B X-ray diffractometer with a $\text{CuK}\alpha$ radiation was used in the X-ray analysis.

B. 1. Identification of Phases

Phase identification was achieved by a comparison of the diffraction data of the calcined product with those given by the ASTM cards.

B. 2. Quantitative Analysis

B. 2. 1. Preparation of Standard Calibration Curves

The standard mixtures were prepared from ferric oxide which was previously used and commercial high purity barium ferrite powder with mixing ratios as shown in Table 1. The material weighed to a tenth of a milligram, mixed in a mortar for 20 minutes, and then diffracted by X-ray diffractometer in the range $2\theta=29^\circ$ to 68° . In this work the line-

to mass absorption effect.⁽⁹⁾

B. 2. 2. Determination of Reaction Amount

The quantitative determinations of the amount of barium ferrite formed were carried out by comparing the diffraction data of calcined samples with standard calibration curves. The average value of the 6 determinations was taken.

Table 1. Constitution of Standard Mixtures

Batch No.	Mixing ratio (in wt%)		Wt. of Sample (gr.)
	BaO·6Fe ₂ O ₃	α-Fe ₂ O ₃	
1	100	0	5
2	90	10	5
3	80	20	5
4	70	30	5
5	60	40	5
6	50	50	5
7	40	60	5
8	30	70	5
9	20	80	5
10	10	90	5
11	0	100	5

intensity technique was used to determine the ratio of intensities, and the average linear background was obtained by considering the fluctuation of the original background at which no peak was appeared. The and prepared data of six 2θ angles having good trend was selected the calibration curves using an arithmetic correction expression⁽⁶⁾

$$(1-K_A)/K_A = \alpha_{AB} (1-C_A)/C_A$$

where K_A is the relative intensity and C_A the weight fraction of component A, and α_{AB} is the value depend on the characteristic line of component A. Figure 1 shows two typical calibration curves for $2\theta=32.2^\circ$ (Ba-Ferrite line) and 33.2° (α -Fe₂O₃ line). The deviations of these curves from the linearity is due

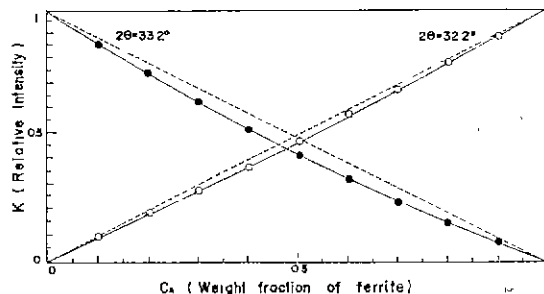


Fig. 1. Standard calibration curves for $2\theta=33.2^\circ$ (α -Fe₂O₃ peak-angle) and $2\theta=32.2^\circ$ (Ba-Ferrite peak-angle) using a CuK α radiation.

III. RESULTS AND DISCUSSION

Figure 2 shows the experimental results for the ferrite formation with time at temperatures from 900° to $1,100^\circ\text{C}$ in the reactions between barium carbonate and ferric oxide. From these kinetic curves it was found that the reactions follow parabolic relationships, indicating that the mechanism of the latter stages might be a diffusion-controlled process. From Fick's law of diffusion in a solid-solid reaction, an equation

$$\alpha = Kt^{\frac{1}{2}}$$

can be derived. Where α is the weight fraction reacted, t the time, and K a reaction rate constant. The plots of the fraction transformed versus the square root time yield linear relationships as shown in Fig. 3. These curves for isothermal heat-treatments indicate the reactions occur predominantly by diffusion-controlled process in the latter stages of the reaction. In Fig. 3, it is found that the straight lines have their ordinate intercepts when they are extrapolated to $t=0$, even though α must be zero when t is zero. A question then arises for the earlier stages of the reaction.

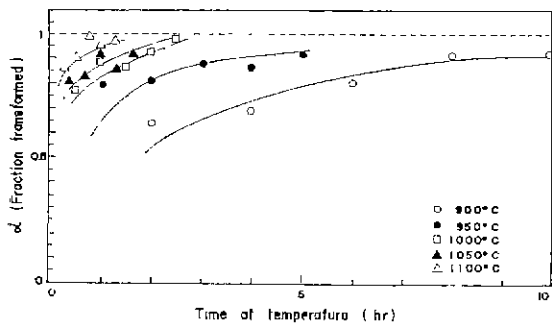


Fig. 2. Reaction of iron oxide-barium carbonate mixture as a function of time at various temperatures

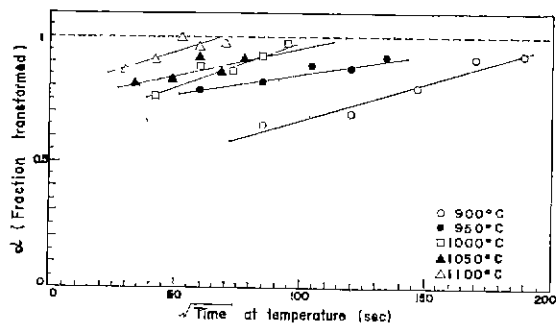
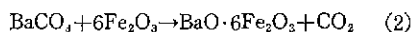
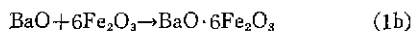


Fig. 3. Reaction of iron oxide-barium carbonate mixture as a function of square root time at various temperatures

This problem cannot be solved by our data because of the very rapid reaction rates at the initial stages. The initial reaction might be controlled by another mechanism such as surface reaction or by diffusion process of different species or by both of them. It is also likely that a very fast surface reaction might be responsible for the observation.

The possible reaction steps in the system of barium carbonate and ferric oxide are:



When the rate of reaction (1b) is much greater than that of reaction (1a), the formation of barium ferrite must be controlled by the decomposition rate of barium carbonate. On the other hand if the rate of reaction (1b) is much less than that of reaction

(1a), the formation must be controlled by the reaction-mechanism of reaction (1b). In the earlier studies, many workers assumed that the liberation of CO_2 gas was an indication that the reaction (1b) had been actually taken place. However, it is a priori not clear that it is so. It is easily conceivable that

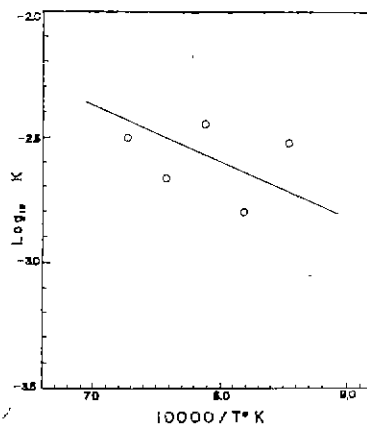


Fig. 4. Rate of formation as a function of temperature for barium ferrite

decomposition of BaCO_3 can occur without any reaction with ferric oxide, as studied by Ward and Struthers.⁽²⁾ If the kinetics is controlled by the reaction (1b) it is quite plausible that the ferrite formation reaction is bulk diffusion-controlled. Indeed, a square root time dependence of reaction rate as shown in Fig 3 at the latter stages supports this interpretation. However, we can not say, for sure, what diffusion or diffusion species is actually responsible for it from this experimental result alone. Any interdiffusion of Ba^{+2} , Fe^{+3} and O^{-2} might be contribute to form barium hexaferrite.

The experimental activation energy for the latter stages of the formation of barium ferrite is 14 ± 10 Kcal, which is calculated from the slope of a plot of logarithm of reaction rate constant versus the reciprocal absolute temperature, Fig. 4. The small activation energy is comparable to that of an earlier work by Ward and Struthers⁽²⁾ and the magnitude of activation energy (14 ± 10 Kcal/mole) seems to be smaller than what one would expect to be an activation energy for bulk diffusion in an oxide system.

IV. CONCLUSIONS

The results of this work may be summarized as follows:

1. In the latter stages of the formation of barium ferrite the reaction is controlled by a diffusion process.

2. In the earlier stages of the formation of barium ferrite the reaction is controlled by a different mechanism. It can be surface reaction, or diffusion process of different species or by both of them.

3. The experimental activation energy for the latter stages of the formation of barium ferrite is 14 ± 10 Kcal/mole.

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