

# Grain Growth in Barium Ferrite

## II. Grain Growth in Barium Ferrite

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### 바륨페라이트내의 입자 성장

#### 제 2 보 바륨페라이트내의 입자 성장

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#### 개 요

본 연구는 다결정질(多結晶質) 바륨 페라이트의 고상간(固相間)의 반응에 있어서 입자성장기구(粒子成長機構)의 규명 및 기타 유용한 자료를 얻고자 수행되었으며 아울러 첨가물(添加物)의 첨가효과도 관찰하였다. 실험은 1150°C 부터 1300°C 까지 25도의 간격으로 행해졌으며 입자성장현상은 전자현미경으로 관찰되었다. 실험결과, 1150°C 부터 1200°C 까지는 식(式)  $D^2 - D_0^2 = Kt$  ( $D$ : 반응이 진행된  $t$  시간후의 입자경(粒子徑),  $D_0$ :  $t=0$  때의 입자경,  $K$ : 반응속도)로 표현되었으며 비교적 고온에서는 증발-응축기구(蒸發-凝縮機構)가 관여됨을 관찰하였다.

한편 실험적으로 구한 활성화에너지(活性化 Energy)는  $130 \pm 20$  Kcal/mole 이었으며 소량의 첨가물  $SiO_2$  는 반응속도를 저하시키나 활성화 에너지에 대해서는 큰 영향을 미치지 못하였다.

### I. INTRODUCTION

The grain growth behavior in ferrites have been received a great amount of attention<sup>(1)(2)(3)</sup> in connection with their properties. During recent years much has been studied about the grain growth in ferrites. However, the grain growth reaction has not been studied in detail for barium ferrite.

The grain growth in polycrystalline barium ferrite was investigated during a solid-state sintering by quantitative measurements of the kinetics. The present

study was extended to observe the influence of impurity on the growth behavior.

In making a model of growth process, an expression deduced by Burke<sup>(4)</sup> shows that the rate of grain growth in polycrystalline body will be inversely proportional to the grain size as given by the following expression

$$\frac{dD}{dt} = \frac{K'}{D}$$

where  $D$  is the instantaneous average grain size,  $t$  the sintering time,  $K'$  a temperature-dependent constant.

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Upon integration this can then be rewritten in following equation:

$$D^2 - D_0^2 = K(t - t_0)$$

where  $D_0$  is the average grain size at time  $t_0$  and  $K$  a reaction constant.

## II. EXPERIMENTAL

### A. Preparation of Samples:

Barium ferrite powder was prepared from reagent-grade barium carbonate and commercial ferric oxide of high purity, which were mixed to form  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ . The physical and chemical properties of the two starting materials and the method of preparation before calcination were described in Paper I. The mixture was calcined at  $1180^\circ\text{C}$  for 3 hours and 20 minutes. The formation of barium ferrite was revealed by X-ray diffraction examination and no second phases were present in the calcined product. The calcined agglomeration was then ground with a pulverizer, passed through a No. 60 U. S. Standard sieve, and wet-milled in a steel ball mill for 96 hours with distilled water. Then after remilling and redrying, the powder was stored in a desiccator before pressing.

A. 1. Undoped Specimens: The powder was cold-pressed at  $2.5 \text{ ton/cm}^2$  into discs 1.5cm. in diameter and 0.5cm. in thickness. The binder of 0.2% polyvinyl alcohol (PVA) aqueous solution was added and the die wall was lubricated with a coating of oleic acid. After pressing, the compacts were heated to  $500^\circ\text{C}$  and cooled down to remove the organic materials. Any appreciable grain growth was not observed by this treatment.

A. 2. Doped Specimens: 1% silicic acid was added to the calcined product and wet-milled together for 96 hours as described in A. The doped specimens were prepared by the same method as mentioned in A. 1.

A. 3. Sintering Condition: Isothermal sintering was run at  $25^\circ\text{C}$  intervals in the temperature range  $1150^\circ$  to  $1300^\circ\text{C}$  for various time at each temperature, in air atmosphere in a resistance-heated box furnace.

Each specimen, after the desired time, was rapidly withdrawn from the furnace and quenched in air. All the temperature were measured by a Pt/Pt-Rh13 thermocouple. The temperature fluctuation in heating zone was  $\pm 3^\circ\text{C}$ .

### B. Electron Microscope Analysis:

A Hitachi HU-125C electron microscope was used in this investigation to study the grain growth phenomena.

B. 1. Measurement of Initial Particle Size: Initial particle size was measured from the calcined powder by dispersing on a copper specimen grid and directly taking electron micrographs.

B. 2. Determination of the Grain Size: The sintered specimens were fractured parallel to their circular plane. The carbon replicas were made for the most of them without polishing and etching. The only several specimens were polished and etched. The etching was carried out in warm concentrated hydrochloric acid for various time to observe the grain structure. Replication for electron microscopy was prepared by a two-stage process, using cellulose acetate and carbon. A cellulose acetate replica was first prepared. The plastic replica was shadowed with platinum-carbon by vapor-deposition in vacuum evaporator. The shadowing angle was  $45^\circ$ . The replica was then placed on a specimen screen and washed with acetone to dissolve the cellulose acetate and to leave the carbon replica. After washing the resulting carbon replica was examined in an electron microscope.

The average grain size was measured by two steps on the assumption that all the grains are spheres of uniform size. Each average traverse length across grains by runs of 5 random lines passing through the electron micrograph of the sample was primarily obtained and then an actual average grain size was obtained by using an equation<sup>(5)</sup>.

$$D = (3/2)\bar{L}$$

Where  $D$  is the actual average grain size and  $\bar{L}$  the average traverse length.

## III. RESULT AND DISCUSSION

The average initial particle size was  $0.4\mu$ . This average value was taken from two determinations by

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measuring two electron micrographs of samples.

In Fig. 1-3, electron micrographs show that the grain increases in size with increasing time and temperature as we expected.

From the results, a plot of  $(D^3 - D_0^3)$  versus  $t$  for isothermal grain growth shows a good linearity at low temperatures and poor at higher temperatures for undoped specimens as shown in Fig. 4. This was also found in  $\text{SiO}_2$ -doped specimens as demonstrated in Fig. 5. The same result was reported by Paulus<sup>(6)</sup> in Ni-Zn ferrite when  $D^2$  was plotted against  $t$ .

The deviation of linearity can be understood by reviewing the development of the theory of grain growth<sup>(4)</sup>, that is,

$$\frac{dD}{dt} = AM\sigma \left( \frac{1}{D} - \frac{1}{D_f} \right) \quad (1)$$

where  $M$  is the grain boundary mobility,  $\sigma$  the

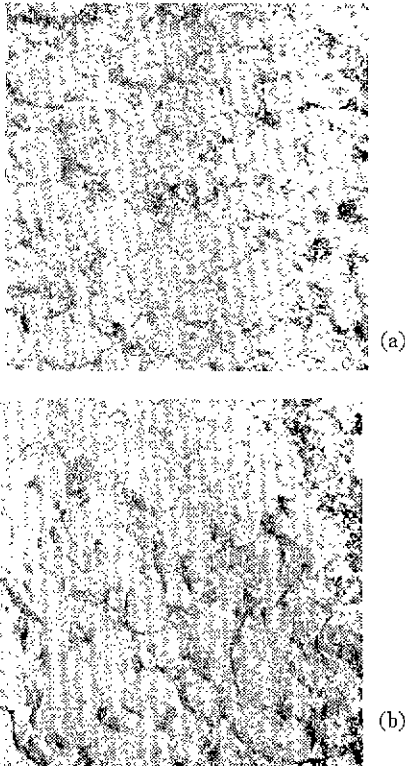


Fig. 1. Grain growth in polycrystalline barium ferrite sintered at 1150°C for  
a. 2 hours (undoped, etched- $\times 5000$ ),  
b. 20 hours (undoped, etched- $\times 5000$ ).

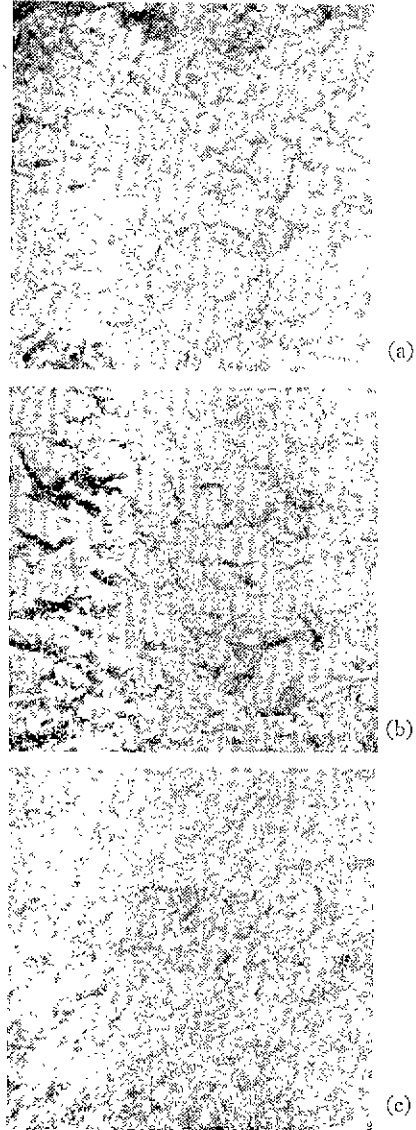


Fig. 2. Grain growth in polycrystalline barium ferrite sintered at 1250°C for  
a. 5 hours (undoped,  $\times 2500$ ),  
b. 8 hours (undoped,  $\times 2500$ ),  
c. 8 hours ( $\text{SiO}_2$ -doped,  $\times 2500$ ).

Spiral growth are shown in the interior grains in a solid circle in Fig. 2-a.

interfacial energy of the boundary,  $A$  a geometrical constant, and  $D_f$  the average limiting grain size when an uniform dispersing of inclusions prevents grain growth. Here  $D_f$  can then be expressed by the relation of Zener<sup>(7)</sup> as

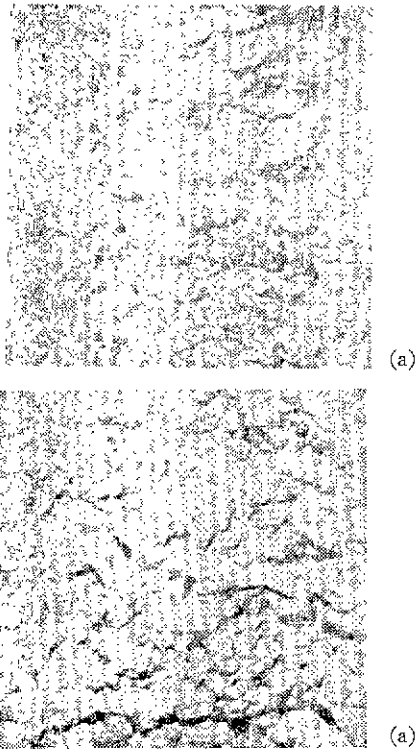


Fig. 3. Grain growth in polycrystalline barium ferrite sintered at 1275°C for 3 hours and 45 minutes  
 a. (undoped, ×2500),  
 b. (SiO<sub>2</sub>-doped, ×2500)

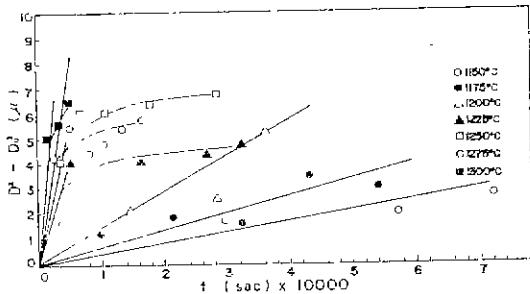


Fig. 4 Isothermal grain growth with sintering time and temperature in undoped polycrystalline barium ferrite

$$D_f = \frac{d}{f} \tag{2}$$

where  $d$  is the average inclusion size and  $f$ , their volume fraction.

In Eq. (1) if the mobility of the grain boundary is greater than the rate of change of  $D_f$ , the over-

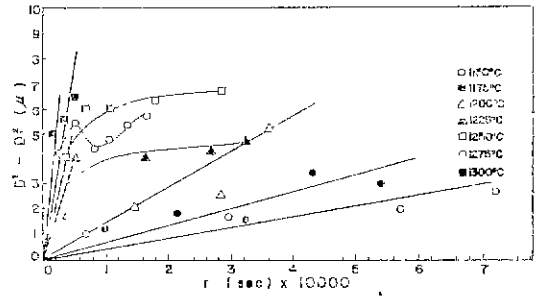


Fig. 5. Isothermal grain growth with sintering time and temperature in SiO<sub>2</sub>-doped polycrystalline barium ferrite

all grain growth rate is controlled by the rate of change of  $D_f$ . And then the grain boundary mobility is increased with increasing temperature because of the consideration of the equation

$$M = M_0 \exp\left(\frac{-Q_b}{RT}\right) \tag{3}$$

Thus, the over-all grain growth rate, at relatively high temperatures, can be decreased and the deviation is increased with time.

Conversely, at low temperatures, grain boundary mobility is much lower than the rate of change of  $D_f$ . Thus the rate of change of  $D_f$  could not affect the over-all growth rate and the rate is mainly determined by the grain boundary mobility. These explanations is one of the reasons why a poor linear relationship yields at high temperatures

Second, these non ideal behavior can be interpreted in terms of mechanisms of growth that occur during sintering. That is; an evaporation-condensation mechanism might be contribute to the decreasing growth-rate. Of course it is impossible to suggest decisively whether a diffusion or an evaporation-condensation might be predominant in the initial stages of growth at high temperature, it can be undoubtedly accepted that the evaporation-condensation mechanism and the rate of growth are related. The observations of the spiral growth in the interior grains under the presence of the saturation of the vapor are a clue to this implication, as seen in Fig. 2-a. A similar observation was reported by Drobek and his co-workers.<sup>(6)</sup>

However a cautious wording is necessary in this regard since spiral growth morphology can be frequently revealed by a thermal etching due to evaporation at high temperature. Therefore we can say unequivocally that evaporation can take place at this temperature range, but it is another matter whether the evaporation mechanism is responsible for the grain growth.

Fig. 6 shows a plot of  $\log K$  versus  $1/T$  for undoped specimens. We obtained the experimental activation energy of  $130 \pm 20$  Kcal. The same analysis was also made for doped specimens and it was found that the activation energy for  $\text{SiO}_2$ -doped specimens were closely similar to that for undoped specimens as shown in Fig. 6. It might perhaps be suggested that the small amount of the grain growth inhibitor,  $\text{SiO}_2$ , does not have an important effect upon the activation energy for grain growth, even though the reaction rate of doped barium ferrite is less than that of undoped barium ferrite. Our experimental result did not agree with a work of MacEwan<sup>(9)</sup> on the grain growth of  $\text{UO}_2$ . He obtained an experimental result of 87 Kcal/mole for the activation energy for grain growth in  $\text{UO}_2$  which is nearly equal to that (88 Kcal) for  $\text{U}^{4+}$  ion self-diffusion. The result is different from the experimental activation energies of zone-refined lead<sup>(10)</sup> where the activation energy for volume self-diffusion is about four times that for grain growth. He interpreted that the nearly equal activa-

tion energy for grain growth in  $\text{UO}_2$  may be due to the presence of isolated pores or of the small impurities (approximately 250 PPM). But it may be doubtful that the presence of isolated pores or of such parts per million of impurities in  $\text{UO}_2$  severely affect the activation energy, although the pre-exponential factor in the Arrhenius relation can be greatly affected. On this basis, the present result may suggest that when the grain growth does not occur rapidly enough, the activation energy for grain growth will be equal to that for solute volume diffusion. If this is the case, we should expect that the activation energy of  $130 \pm 20$  Kcal/mole for the grain growth in this experiment will be equal to that of one of diffusing ions in barium hexaferrite. Unfortunately however, no diffusion data are available for a direct comparison.

#### IV. CONCLUSIONS

1. At relatively low temperature, between 1150° and 1200°C the grain growth reaction can be described by an equation modified by Burke for a long time.
2. At higher temperature, there is an indication that a vapor transport mechanism is also taking place.
3. The activation energy for the grain growth process in polycrystalline barium ferrite is  $130 \pm 20$  Kcal/mole. No significant difference in the activation energy between the undoped and  $\text{SiO}_2$ -doped barium ferrite was found, even though the reaction rate of doped barium ferrite is less than that of undoped barium ferrite.

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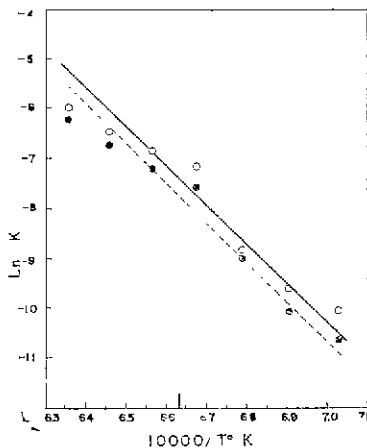


Fig. 6. Rate of grain growth as a function of temperature for barium ferrite

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