Ceramics International 27 (2001) 215–218

CERAMICS INTERNATIONAL

Effect of grain orientation on abnormal grain growth in Ba-hexaferrite

Yoon-Chul Lee, Sang-Yeup Park *, Moon-Ki Choi, Sang-Ok Yoon

Department of Ceramic Engineering, Kangnung National University Kangnung, Kangwondo 210-702, South Korea

Received 21 February 2000; received in revised form 20 March 2000; accepted 19 April 2000

Abstract

The nucleation and growth behavior of Ba-hexaferrite has been observed and explained in terms of grain orientation due to liquid phase. It has been observed that the nuclei formation for abnormal grain growth was driven by the capillary force due to the liquid phase. A strong orientation of small grains was observed within abnormal grains in materials obtained using BaB_2O_4 as a sintering aid. The microstructural orientation of Ba-hexaferrite observed in this study was in good agreement with the X-ray diffraction analysis based on the peak intensity of the (107) plane.

Keywords: Grain orientation; Abnormal grain growths; Ba-hexaferrite

1. Introduction

As a hard ferrite, Me-hexaferrite (Me = Ba, Sr, Pb) is used for permanent magnets [1]. In hard ferrites, abnormal grain growth is known to be harmful to densification and coercive force, because of pore entrapment inside grains during rapid grain growth [2]. On the other hand, abnormal grain growth has been applied to the useful application of microstructure texturing due to grain alignment [3,4]. For example, the high degree of grain orientation as a consequence of abnormal grain growth has been reported in sintering of Ba-hexaferrite [5].

Abnormal grain growth of hard ferrite has been associated to such as the influence of a liquid phase [6], the size distribution of starting powder [7], and also a fast heating rate [2]. Despite that, the main cause of the abnormal grain growth of hard ferrite is known to be the liquid phase, the exact role of the liquid phase is still somewhat unclear. As a strong possibility, the liquid phase will provide a fast diffusion path compared to grain boundary or lattice diffusion in solid state sintering. In many studies on abnormal grain growth, only the growth stage has been of great concern compared to the nucleation stage, because of fast appearance and rapid growth of nuclei during abnormal grain growth. Recently, it has been reported that the nucleation process and particle rearrangement is important for the occurrence of abnormal grain growth [8,9]. The purpose of the present work is to investigate the effect of grain orientation on abnormal grain growth in Ba-hexaferrite. The observed abnormal grain growth was explained in terms of nuclei formation and grain rearrangement due to liquid phase.

2. Experimental

Starting powders were reagent grade Fe_2O_3 and $BaCO_3$. BaB_2O_4 used as a sintering additive was prepared from the calcination of $BaCO_3$ and B_2O_3 powder mixtures at 700°C for 1 h. Because of the densification problem encountered in the specimens with stoichiometric composition of $BaO6Fe_2O_3$, the compound BaO5.5-Fe_2O_3 and BaB_2O_3 as sintering additives, were used in order to obtain fully dense specimens of $BaO6Fe_2O_3$. The powder mixtures were ball-milled for 24 h in a Teflon jar in distilled water, dried in an oven, and then calcined at 700°C for 2 h. Powders were granulated with the addition of PVA and pressed into billets of 10 mm diameter under 98 MPa. Powder compacts were calcined at 600°C for 2 h for the burn-out of PVA and sintered in air at various temperatures and times at

* Corresponding author. Tel.: +82-391-640-2363; fax: +82-391-640-2244.

E-mail address: sypark@knusun.kangnung.ac.kr (S.-Y. Park).

0272-8842/01/$20.00
PII: S0272-8842(00)00067-5

constant heating and cooling rate of 10°C/min. In order to reveal the microstructure, specimens were polished and thermally etched at 1000°C. The chemical composition of grains was determined by EDS microanalysis.

3. Results and discussion

Sintered density of $BaO5.5Fe_2O_3$ containing BaB_2O_3 specimens showed near theoretical density(5.3 g/cm^3), whereas specimens of $BaO6Fe_2O_3$ without additive were less dense as shown in Fig. 1. Because the intermediate compounds such as $2BaOFe_2O_3$ and $BaOFe_2O_3$ can be dissociated by unreacted $BaCO_3$, the addition of BaB_2O_3 was effective for the densification of Ba-hexaferrite by the reduction of unreacted $BaCO_3$.

In contrast to the advantage of BaB_2O_4 for densification, most of specimens sintered with BaB_2O_4 showed abnormal grain growth, as shown Fig. 2. The abnormal grain growth started at 1080°C and prevailed at increased sintering temperature and time. It appears quite similar to the typical abnormal growth in the presence of a liquid phase. Thus, it is believed that the small amount of liquid phase in BaB_2O_3 added specimens plays an important role for the occurrence of abnormal grain growth by providing a fast diffusion path between solid grains. The absence of abnormal grain growth during sintering below 1800°C may support this hypothesis.

Fig. 3 shows an abnormal grain with a well faceted hexagonal shape. It has been frequently observed that abnormal grain growth occurs in systems with anisotropic interfacial energy. For grains of faceted shape, a different grain growth rate is expected to occur depending on the anisotropy of the crystal plane. Several studies have been performed on high anisotropy systems such as Sr-hexaferrite with magnetoplumbite structure and alumina with hexagonal structure [2,10] to find the origin of abnormal grain growth. Recently, Park and Yoon [11] proposed that the abnormal grain growth in systems with faceted crystal planes could be explained by a 2-dimensional nucleation mechanism in terms of the critical size. As an important criterion of their suggestion, some large grains over the critical size were formed or were pre-existing in the microstructure for the initiation of abnormal grain growth. Although they provide a good criterion for abnormal grain growth,

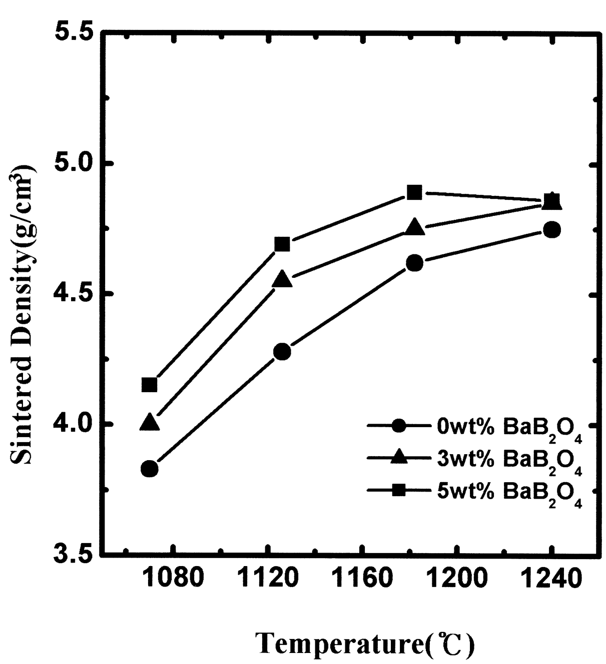

Fig. 1. Density of Ba-hexaferrite as a function of sintering temperature.

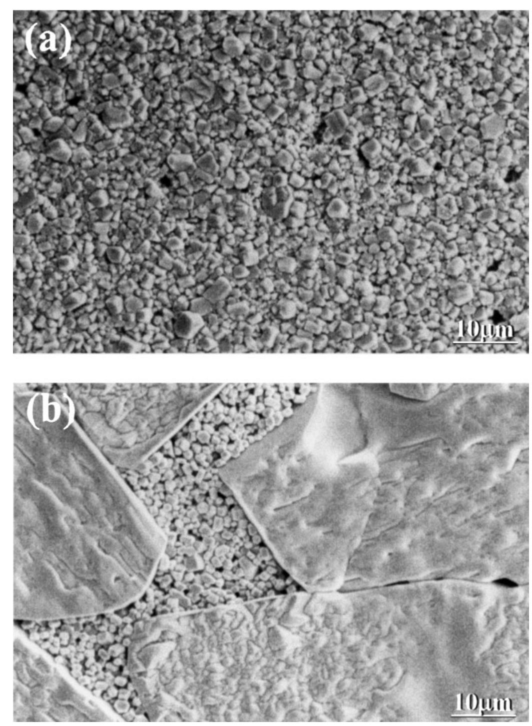

Fig. 2. Microstructures of Ba-hexaferrite (a) without and (b) with 5 wt.% BaB_2O_4. Specimen sintered at 1130°C for 2 h.

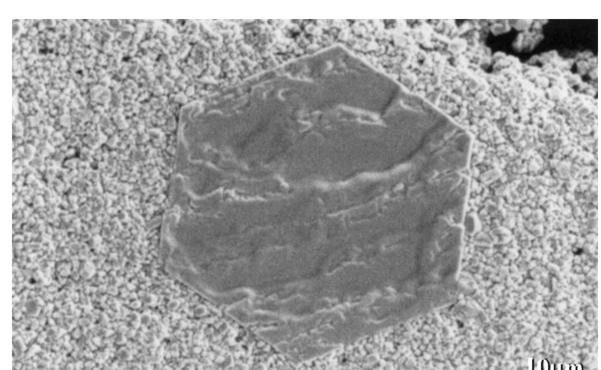

Fig. 3. Abnormally grown Ba-hexaferrite grain showing a well developed hexagonal shape. Specimen sintered at 1130°C for 0 h.

this criterion has a limitation for the explanation of nuclei formation in abnormal grain growth.

As an interesting phenomenon, it was first observed that the abnormal grain growth also has a nucleation stage as shown in Fig. 4. It can be clearly observed that the nuclei are composed of small grains with similar grain size in the matrix. With increasing sintering time, abnormal grains with hexagonal shape were formed firstly (Fig. 3), then the abnormal grains departed from their well faceted shape, and finally appeared in an elongated shape with grain impingement, as shown in Fig. 5. Except for the nucleation stage, such a type of abnormal growth is quite similar to a typical abnormal growth in other systems. Furthermore, well orientated small grains were observed inside the large grains, as shown in Fig. 5.

From the above observations, it is believed that the abnormal grain is formed by grain rearrangement, which is accompanied by grain rotation. Considering the small hexagonal grains in the matrix, grain rotation and rearrangement is expected to occur towards their hexagonal face. This face to face contact due to the liquid phase might be increased with sintering temperature and time. In the presence of a small amount of liquid phase, the small grains remain in contact with each other due to the capillary force between grains. In turn, small grains will be sliding or rotating in order to maintain the low energy position. If the grains have a well faceted shape or small size, grain rearrangement will occur more easily. In a well faceted grain with a high anisotropic orientation, a small area of crystal planes will have high interfacial energy, whereas crystal planes with large areas will have a low interfacial energy due to the equilibrium shape concept based on the interfacial energy minimization condition. Thus, grains can align depending on their interfacial energy, i.e. crystal planes with high interfacial energy will be in contact with each other, and crystal planes with low interfacial energy will be in contact with each other.

In general, the growth rate of crystal planes with high interfacial energy would be faster than for those with low interfacial energy. Therefore, grain growth will proceed in the direction of the fast growing plane due to the orientation of small grains in an abnormal grain. During grain rearrangement, the liquid phase squeezed out between the grains will promote further grain growth and reshaping of the abnormal grain. This proposed abnormal growth process is somewhat similar to the classical liquid phase sintering concept, i.e. particle rearrangement and solution-reprecipitation [12]. It is

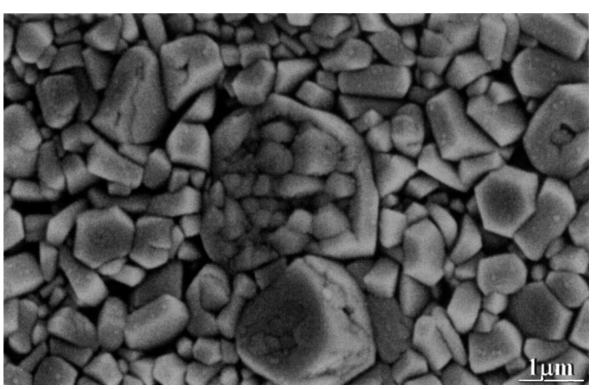

Fig. 4. Nuclei for abnormal grain growth observed in Ba-hexaferrite with 5 wt.% BaB_2O_4. Specimen sintered at 1030°C for 2 h.

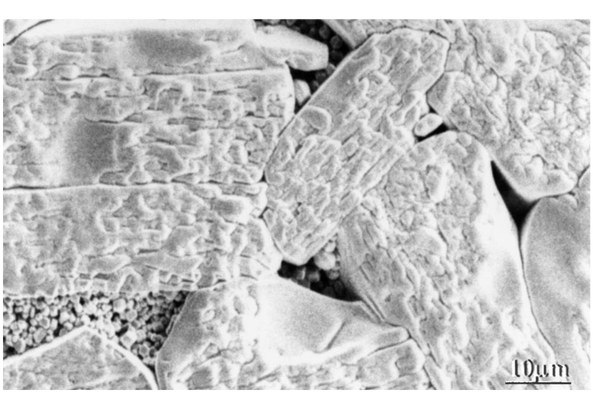

Fig. 5. SEM micrograph of abnormal grains with impingement. Small grains were well oriented inside an abnormal grain. Specimen sintered at 1130°C for 12 h.

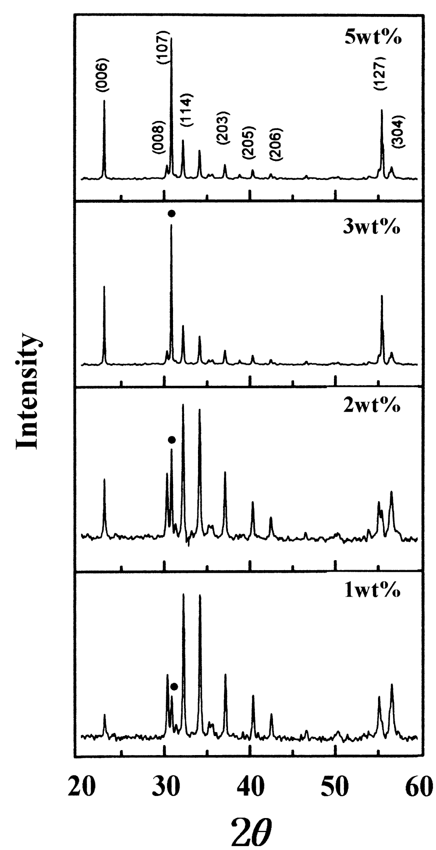

Fig. 6. Changes of X-ray peak intensity of the (107) plane with increasing the BaB_2O_4 addition. Specimen sintered at 1130°C for 2 h.

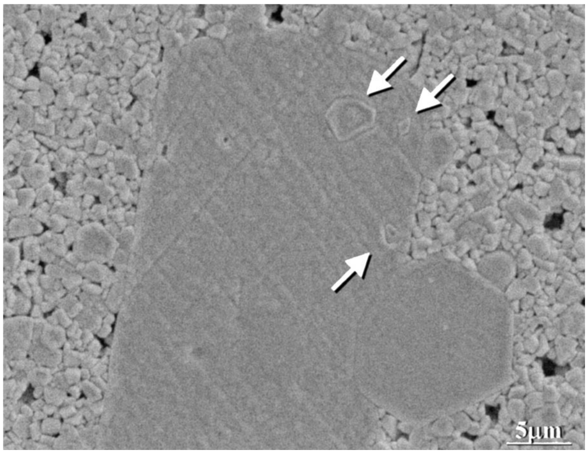

Fig. 7. Microstructures of Ba-hexaferrite sintered at 1130°C for 12 h. Arrows indicate small grains trapped inside of abnormal grain.

believed that the reshaping of the abnormal grain might be influenced by the solution reprecipitation process.

Fig. 6 shows the X-ray diffraction patterns for specimens containing abnormal grains at increased BaB_2O_4 content. The peak intensity of the (107) plane increased for specimens sintered at increased temperature and additive content. This suggests that abnormal grain growth occurred toward (107) planes due to the successive orientation of small grains. Despite such grain orientation not being observed in some of the large grains, it is expected that the inside of these large grains also contained oriented grains from the prediction of fracture surface as shown in Fig. 5.

The grain trapped inside a large grain, indicated by the arrow in Fig. 7, has been identified as the same phase by EDS microanalysis. The observed grain entrapment is expected to occur as a consequence of rapid boundary migration during the reshaping process of abnormal grain. This grain entrapment is not confined only in the Ba-hexaferrite system. In Mn–Zn ferrite and Y–Ba–Cu–O ceramics [13], the same phenomenon was observed during abnormal grain growth.

4. Conclusions

The liquid phase due to the addition of BaB_2O_4 in Ba-hexaferrite appears as the main cause for the occurrence of abnormal grain growth. It has been first observed that the grain rearrangement due to liquid phase is a critical condition for the formation of nuclei during abnormal grain growth. As a clue for the grain rearrangement, a strong texturing of small grains occurs in an abnormal grain with an increase in the BaB_2O_4 content. This texturing effect was also confirmed by the peak intensity of the (107) plane in X-ray diffraction analysis.

References

[1] H. Harada, The recent progress of hexagonal ferrite magnets, in: T. Yamaguchi, M. Abe (Eds.), Ferrite Proceeding of the ICF-6, The Jpn. Soc. of Powder and Powder Metallurgy, 1992, pp. 1122–1126.

[2] H.H. Yoon, D.-Y. Kim, Effect of heating rate on the exaggerate grain growth during the sintering of Sr-hexaferrite, Mater. Lett. 20 (1994) 293–297.

[3] H. Watanabe, T. Kimura, T. Yamaguchi, Sintering of platelike bismuth titanate powder compacts with preferred orientation, J. Am. Ceram. Soc. 74 (1) (1991) 139–147.

[4] M.M. Seabugh, I.H. Kerscht, G. Messing, Texture development by templated grain growth in liquid phase sintered -alumina, J. Am. Ceram. Soc. 80 (5) (1997) 1181–1188.

[5] A.L. Stuijts, Sintering of ceramic permanent magnetic materials, Trans. Brit. Ceram. Soc. 55 (1956) 57–62.

[6] C. Kooy, Anisotropic exaggerated grain growth and sintering in Mn–Fe_2O_4 and $Y_3Fe_5O_{12}$, in: Science of Ceramics, Vol. 1, Academic Press, New York, 1982, pp. 21–34.

[7] S. Besenicar, M. Drofenik, D. Kolar, in: C. M. Srivataya, M. J. Patini (Eds.), Advances in Ferrite, Oxford and IBH Publishing, New Delhi, India, 1989, pp. 163–167.

[8] V.V. Novikov, Rate of nucleation growth of coarse crystallites during the abnormal grain growth, Z. Metallkd 89 (11) (1998) 767–771.

[9] H.S. Ryoo, S.K. Hwang, Anisotropic atomic packing model for abnormal grain growth mechanism of WC–25 wt.% Co alloy, Scripta Mater. 39 (11) (1998) 1577–1583.

[10] H. Song, R.L. Coble, Origin and growth kinetics of platelike abnormal grains in liquid phase sintered alumina, J. Am. Ceram. Soc. 73 (7) (1994) 2077–2085.

[11] Y.S. Park, N.M. Whang, D.Y. Yoon, Abnormal grain growth of faceted (WC) grains in a (Co) liquid matrix, Metall. Mater. Trans. 27A (1996) 2089–2819.

[12] H. S. Cannon and F. V. Lenel, Some observations on the mechanics of liquid phase sintering, in: Pulvermetallurgie (Plansee Proceedings 1952), F. Benesovsky (Ed.), Metallwerk Plansee GmbH, Reutte, 1953, pp. 106–122.

[13] I.K. Jung, D.Y. Kim, Z.G. Khim, S.J. Kwon, Exaggerated grain growth during the sintering of Y–Ba–Cu–O superconducting ceramics, Mater. Lett. 8 (3) (1989) 104–107.