



PERGAMON

Scripta mater. 44 (2001) 2525–2529



www.elsevier.com/locate/scriptamat

TEXTURED MICROSTRUCTURES IN BARIUM HEXAFERRITE BY MAGNETIC FIELD ASSISTED GELCASTING AND TEMPLATED GRAIN GROWTH

David B. Hovis and K.T. Faber

Department of Materials Science and Engineering, Robert R. McCormick School of Engineering and Applied Science, Northwestern University, Evanston, IL 60208, USA

(Received September 27, 2000)

(Accepted December 27, 2000)

Keywords: Templated grain growth; Casting; Microstructure

Introduction

Textured ceramic microstructures can often provide near single crystal properties without the difficulties associated with forming single crystals. (1,2) The processing techniques for producing textured structures are somewhat limited, however. Traditional methods for forming textured microstructures include starting with anisotropic powders and aligning them with either compaction forces (uniaxial pressing) (3) or viscous shear forces (tape casting) (4).

More recently, templated grain growth (TGG) has been developed to provide a simpler method of creating textured ceramic microstructures. (1,3–5) TGG requires only about 5% of the initial powder to be anisotropic, with fine isotropic powder forming the surrounding matrix. The anisotropic “seed” particles can be aligned by standard processing methods. During final sintering the seeds grow and consume the surrounding matrix, producing a highly textured microstructure.

One shortcoming of both traditional texturing methods and traditional TGG processing is that the texture direction is entirely determined by the mechanical forces during processing. In uniaxial pressing the texture is perpendicular to the pressing direction and in tape casting the texture is parallel to the direction of tape casting. It would be desirable to have a processing method in which the texture direction is not directly coupled to mechanical forces, allowing a wider range of shapes and sizes to be textured.

Magnetic field assisted gelcasting is a proven candidate for producing textured microstructures. (6,7) In the basic gelcasting technique, a ceramic powder is suspended in a monomer solution to form a slurry. An initiator and catalyst are added and the slurry is poured into a mold. A polymerization reaction takes place which forms a solid gel and locks the particles in place for the remainder of processing. Standard ceramic powder processing techniques may then be used complete densification. This technique is enhanced by applying a magnetic field to the slurry prior to full polymerization. If the powder in the slurry is magnetically anisotropic, the easy magnetization direction will align with the magnetic field and then be held in place by the polymer gel network. This strategy alone, however, is not sufficient for texturing all magnetically anisotropic materials, as described here for barium hexaferrite.

Textured barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$, also known as barium ferrite) is commonly used in permanent magnets and displays large variations in mechanical properties depending on the texture

orientation.(2) It is a hexagonal (M-Type magnetoplumbite) ferrimagnetic ceramic with the easy magnetization direction along the c-axis. Similar to other hexagonal ceramics, it will readily form plate-shaped powders and grains with the c-axis perpendicular to the plate face. Consequently, barium hexaferrite plates will align perpendicular to an applied magnetic field. However, barium hexaferrite in suspension, by virtue of its ferrimagnetism, will form stacks of plates. Free flowing suspensions of the stacked plates are limited to a volume loading of 15% or less, whereas gelcasting requires a much higher volume loading to avoid drastic volume changes during drying, burnout, and densification. (8,9)

The objective of this paper is to describe a method of producing textured barium hexaferrite by magnetic field assisted gelcasting while avoiding the limited solids loading caused by stacking of barium hexaferrite plates. We illustrate here a method of gelcasting a matrix of non-magnetic iron (III) oxide and barium carbonate in the presence of barium ferrite seeds for templated grain growth. At high temperatures, the iron oxide and barium carbonate react to form a fine-grained barium ferrite matrix surrounding the previously aligned barium ferrite seeds.

Experimental Procedure

Two components are needed in order to make textured barium hexaferrite by combined magnetic field assisted gelcasting and TGG techniques. First, a non-magnetic precursor to barium hexaferrite must be developed that can meet the suspension requirements of gelcasting. Second, seed particles must be produced that are sufficiently anisotropic to serve as templates for texturing.

A non-magnetic matrix which will convert to barium hexaferrite was developed by gelcasting a mixture of Fe_2O_3 (99.95%, $\sim 0.5\mu\text{m}$, All-Chemie) and BaCO_3 (99.8%, $\sim 1\mu\text{m}$, Alfa Aesar, Ward Hill MA) (10). The $\text{Fe}_2\text{O}_3:\text{BaCO}_3$ molar ratio was 5.6:1 with 1.5% by mole of B_2O_3 (as boric acid) was added as a reaction aid.(11) The gel system was 20% by weight solution of hydroxymethylacrilamide (HMAM) (Aldrich, Milwaukee WI) initiated with approximately $0.5\mu\text{L/g}$ slurry of ammonium persulfate (APS) and tetramethylethylenediamine (TMED) (Aldrich, Milwaukee WI). (12,13) The solids loading was 40% by volume. Surfynol CT-131 (AirProducts, Allentown PA) was used as the surfactant. The slurries were ball milled in a HDPE bottle with 3/8" $\text{ZrO}_2\text{-3}\%\text{MgO}$ milling media (Zirconia Inc., Solon OH) for 24 hours. The gels were heated to approximately 50°C to accelerate polymerization. All the gels were cast into chrome-plated brass molds approximately 15mm in diameter and 5mm deep. All gels were dried in air for 24 hours and the polymer was slowly burned out. The samples were isopressed at 275 MPa and then heated at $10^\circ\text{C}/\text{min}$ to 1150°C for 2 hours.

Anisotropic "seed" particles were produced using molten salt synthesis (MSS). (14,15) In this case a two-stage MSS process was needed to produce suitable template particles. Based on previous TGG work on alumina, $10\mu\text{m}$ was chosen as the target size for these particles. (5) First, Fe_2O_3 and BaCO_3 were mixed with KCl as the fluxing agent at a 1:1 reactants:salt weight ratio. Heating to 900°C for 8 hours in an Al_2O_3 crucible produced plate-shaped $\text{BaFe}_{12}\text{O}_{19}$ particles approximately $1\mu\text{m}$ in diameter.

To coarsen the particles, the $\text{BaFe}_{12}\text{O}_{19}$ plates from the KCl melt were mixed with BaCl_2 and Fe_2O_3 . The $\text{BaCl}_2:\text{Fe}_2\text{O}_3$ ratio was 2:1 by weight and the $\text{Fe}_2\text{O}_3:\text{BaFe}_{12}\text{O}_{19}$ ratio was 500:1 by mole. Heating to 1150°C for 8 hours produced particles ranging from $5\text{--}25\mu\text{m}$ and approximately $1\text{--}2\mu\text{m}$ thick. These were deemed adequate for templated grain growth and are shown in Figure 1.

Three types of samples were made. First, gels were cast with only the $\text{Fe}_2\text{O}_3/\text{BaCO}_3$ mixture ("matrix" samples). A second set of samples were made by substituting barium hexaferrite "seeds" for 5% by volume of the $\text{Fe}_2\text{O}_3/\text{BaCO}_3$ mixture used in the matrix samples ("control" samples). A third set of samples were identical to the control samples, but a 1kG permanent magnet was placed on top of the mold during polymerization of the gel ("magnetically-aligned" samples). The magnetic field was parallel to gravity. All other processing conditions were identical as described earlier.

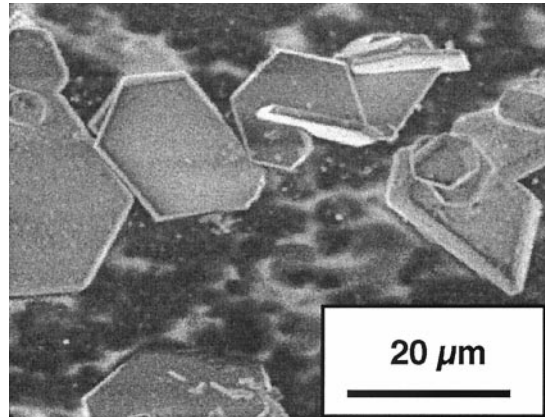


Figure 1. Molten salt synthesized “seed” particles of barium hexaferrite.

After firing the control and magnetically-aligned samples were cross-sectioned and polished. Microstructures were examined using SEM after thermal etching at 1100°C for 15 minutes. X-ray diffraction was used for phase analysis on the matrix samples and for texture analysis on the control and magnetically-aligned samples.

Results

Figure 2 shows x-ray powder diffraction patterns (Cu-K α , XDS2000, Scintag, Cupertino CA) of the as-cast and fired matrix samples indicating that the desired phase has formed and no residual reactants are present. However, a small amount of a second phase, identified from JCPDS card #85–0852 as BaFeO₃, has formed due to an excess of BaCO₃. This is unexpected, because the intermediate phase that is formed during the reaction of Fe₂O₃ and BaCO₃ is believed to be BaFe₂O₄(10).

SEM micrographs of the control and magnetically-aligned samples can be seen in Figure 3a and Figure 3b respectively. The control samples possess a large grain size (\sim 20–30 μ m), but not the plate-like shape indicative of textured barium hexaferrite. The magnetically-aligned samples possess a large grain size (\sim 25–50 μ m), plate-like shape, and a definitive preferred orientation. Stereological

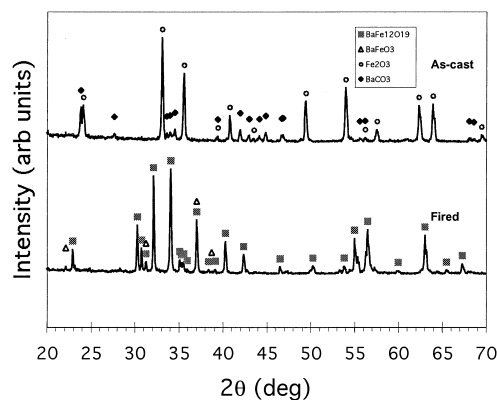


Figure 2. X-ray analysis of the matrix in the as-cast and fired states.

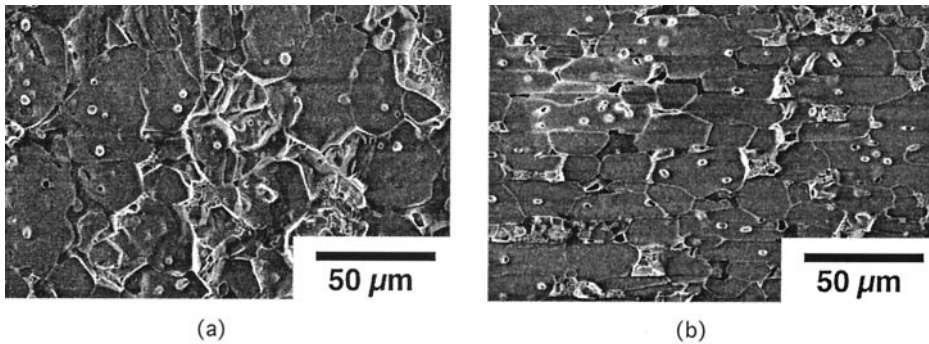


Figure 3. 2 kV FE-SEM images of (a) control and (b) magnetically aligned samples.

imaging was used to assess the morphological texture of the materials. NIH Image 1.62 (National Institutes of Health, Bethesda MD) was used to fit an ellipse to each large grain. The area of each grain and the angles formed between the major axis of the ellipse and the sample surface were recorded. If the angle between the major axis and the sample surface was within $\pm 10^\circ$, the grain was considered “textured.” For a truly isotropic sample, 20 out of every 180 grains or 11%vol would fall into this category. For the control sample, only $3 \pm 1\%$ vol (at 95% confidence) of the microstructure was composed of large grains oriented within $\pm 10^\circ$ of the sample. For the magnetically-aligned material, an average of $54 \pm 4\%$ vol (at 95% confidence) of the material consisted of plate-like grains which were oriented within 10° of the sample surface, indicating a highly textured material. This suggests that the control sample has little, if any, texture and the magnetically-aligned sample is highly textured.

Figure 4 shows a portion of the x-ray diffraction pattern for the intact specimens of the control and magnetically-aligned samples. The two peaks in this region are the basal plane peak (008) and the prismatic peak (110). The ratio of the integrated intensities $I_{110}:I_{008}$ should be 3:1 according to JCPDS card #43-0002. For the control sample, this ratio for the approximate integrated intensities is 8:1, though due to peak overlap, only approximate integrated intensities can be obtained. For the magnetically-aligned sample, the ratio is 1:40. These measurements indicate a high degree of texture for the

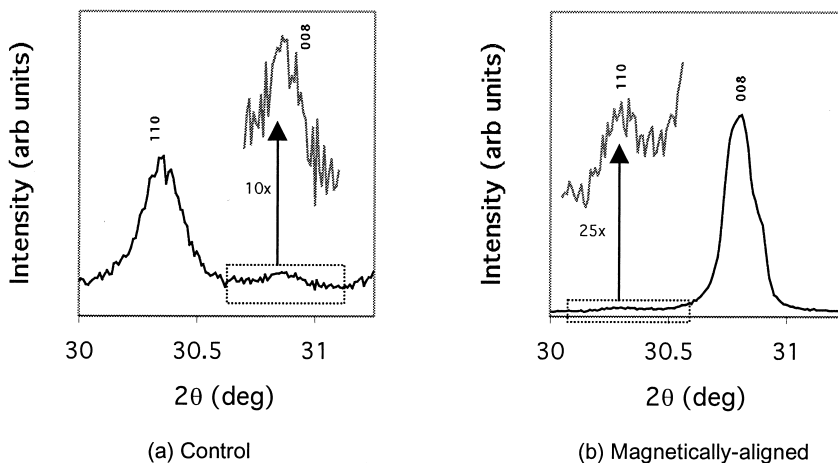


Figure 4. Relative intensities of the (110) and (008) peaks in the control and magnetically aligned samples (Note difference in amplification of smaller peak).

magnetically-aligned sample, consistent with the morphological texture assessment. Texture in the control sample is small and orthogonal to the texture direction in the magnetically-aligned samples, though the mechanism of this is unclear.

Conclusion

Stereological and x-ray diffraction indicate that magnetic field assisted gelcasting using a seeded reactive matrix and templated grain growth can be used to produce highly textured materials in the barium hexaferrite system. This technique provides more flexibility for producing textured microstructures than tape casting or uniaxial pressing. Since the texture direction is coupled only to the direction of the applied magnetic field, a wide variety of sizes and shapes of textured components are afforded. It is anticipated that this technique can be employed for a variety of magnetically anisotropic materials.

Acknowledgments

This work is supported by the National Science Foundation under grant #DMR-9800257. Thanks to John Montgomery and Y. Jennifer Su for their helpful suggestions. Thanks to Thomas Rosenbaum of the University of Chicago for magnet strength measurements. Thanks to D. Lynn Johnson for helpful discussions.

References

1. T. Carisey, I. Levin, and D. G. Brandon, *J. Eur. Ceram. Soc.* 15, 283 (1995).
2. M. Iwasa, E. C. Liang, and R. C. Bradt, 64, 390 (1980).
3. E. Suvaci, M. M. Seabaugh, and G. L. Messing, *J. Eur. Ceram. Soc.* 19, 2465 (1999).
4. T. Carisey, A. Laugierwerth, and D. G. Brandon, *J. Eur. Ceram. Soc.* 15, 1 (1995).
5. M. M. Seabaugh, I. H. Kerscht, and G. L. Messing, *J. Am. Ceram. Soc.* 80, 1181 (1997).
6. M. H. Zimmerman, K. T. Faber, and E. R. Fuller, *J. Am. Ceram. Soc.* 80, 2725 (1997).
7. D. M. Baskin and K. T. Faber, *J. Jpn. Inst. Met.* 61, 1306 (1997).
8. N. S. Walmsley, G. N. Coverdale, R. W. Chantrell, D. A. Parker, and P. R. Bissell, *J. Phys. D-Appl. Phys.* 31, 1652 (1998).
9. R. Muller, R. Hiergeist, H. Steinmetz, N. Ayoub, M. Fujisaki, and W. Schuppel, *J. Magn. Magn. Mater.* 201, 34 (1999).
10. H. P. Steier, J. Requena, and J. S. Moya, *J. Mater. Res.* 14, 3647 (1999).
11. O. T. Ozkan, H. Erkalfa, and Yildirim, *J. Eur. Ceram. Soc.* 14, 351 (1994).
12. M. A. Janney, O. O. Omatete, C. A. Walls, S. D. Nunn, R. J. Ogle, and G. Westmoreland, *J. Am. Ceram. Soc.* 81, 581 (1998).
13. J. K. Montgomery and K. T. Faber, *Scripta Mater.* 42, 283 (2000).
14. R. H. Arendt, 8, 339 (1973).
15. J. Park, D. Lee, H. Shin, and B. Lee, *J. Am. Ceram. Soc.* 79, 1130 (1996).