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Effect of Aggregates on the Microstructure in Manganese Zinc Ferrite

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ABSTRACT

To study the effect of aggregates on the microstructure of sintered bodies, Mn-Zn ferrite powders were prepared by an alcoholic dehydration method. Aggregate powders and reground powders were used as seeds and matrices, respectively. The mixing ratios for the aggregate and reground powders were varied with the sintering temperatures. Green densities were measured with changes in forming pressure and they were related to the microstructures of the sintered bodies. The aggregates proved to be capable of acting as seeds for abnormal grain growth. When the green density difference between the aggregate and the matrix was large, the aggregate could become the seed of abnormal grain growth. As the forming pressure increased, the more aggregates became seeds of abnormal grain growth.

Key words : ***Mn-Zn ferrite, Aggregate, Green density, Microstructure, Abnormal grain growth***

1. Introduction

The early stage of an abnormal grain growth has been of interest for recent years. It has been thought that a substantially larger than average grain grows rapidly by consuming the surrounding normal grains. Chol[1] reported that the distribution of the milled particle size is closely related to the abnormal grain growth during sintering of Mn-Zn ferrites. Yan and Johnson[2] explained that the abnormal grain growth is sustained by the diffusion of Ti into the Mn-Zn ferrite. Sainamthip and Amarakoon[3] investigated the role of a zinc atmosphere on the microstructural development of Mn-Zn ferrite prepared by alcoholic dehydration. He explained that zinc volatilization is the origin of strict microstructural control through abnormal grain growth. Few studies, however, have dealt with the relationship between aggregates and abnormal grain growth.

The presence of aggregates retards compaction at all stages of sintering. Dynys and Halloran[4] reported that alumina powders with the controlled amounts of aggregates exhibited the isothermal shrinkage rates that decreased markedly with increasing in aggregate content. Moreover, the microstructures of aggregated compacts were inhomogeneous, with intraaggregate voids that could be eliminated readily, leading to locally dense regions within the aggregates. Rhodes[5] showed that the elimination or reduction in size of aggregates without an increase in green density also improved sintering behavior. Lange and Metcalf[6] calculated the internal stress from the differences in green density between the aggregate and the matrix during sintering and investigated the effect of aggregates on sintering. These works showed that an initial crack created by the stress from differential sintering acted as the origin of the fracture. However, there have been few reports about the relation between aggregate and abnormal grain growth in microstructure.

In the present study, the microstructures of sintered bodies at various temperatures were examined in relation to variations in seed amounts. The forming pressure was also changed with the seed amounts to establish a relationship between aggregate and abnormal grain growth. Changes in the forming pressure caused changes in the green densities of the matrix as well as the stresses around the aggregate.

2. Experimental Procedure

Mn-Zn ferrite powders were prepared by alcoholic dehydration.[7] The selected composition was $(Mn_{0.57}Zn_{0.32})Fe_{2.11}O_4$, reported to be a low-loss material. The aggregated powder was put into a ball-milling container with a ratio of powder : steel sphere : distilled water = 1 : 9 : 10. The sample then was reground at 130 rpm for 20 h and dried at 100°C for 10 h for the matrix. The reground and aggregated powders were mixed in an alumina bowl. The amounts of aggregated powders were added by 0, 5 10, 15, 20 and 100 wt%. The mixed powder (0.9 g) was compacted into a cylindrical mold of 10 mm in diameter by hand and isostatically compressed by pressure ranging from 20 to 200 MPa.

The formed bodies were heated at a rate of 300°C/h to

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800°C and held for one hour at 800°C. The samples then were heated at a rate of 100°C/h to the sintering temperature range (1200°C to 1350°C) and held there for two hours. During the firing, nitrogen was supplied for 30 min and air for 1.5 h. Finally, the pellets were cooled down to 1000°C, held for 30 min and further cooled down to room temperature in the nitrogen atmosphere.

The morphologies of both the aggregate and the matrix powders and the microstructures of the sintered bodies were observed by Scanning Electron Microscopy(SEM) (model, JSM-5400, Jeol, Japan). The particle size distributions and the specific surface areas of both powders were measured by a centrifugal particle size analyzer (SA-CP3, Shimadzu, Japan) and by gas adsorption (Omnisorp 100 BET, Coulter, U.S.A.) respectively. The phases of the calcined powder were identified by X-Ray Diffraction(XRD); (MO3XHF, Mac, Japan). The green densities of the formed bodies were measured using a dimensional method, while the sintered densities were determined by an Archimedes method.

3. Results and Discussion

Fig. 1 shows SEM photographs and particle size distributions of (a) reground powders (wet-milled for 20 h) and (b) the aggregate powders. Specific surface areas were 5.8 and 2.7 m^2/g, respectively. Although the specific surface area decreased because of necking between the primary particles in the case of (b), the SEM photographs reveal no discernible differences in size between (a) and (b). The primary particles of the matrix and aggregate powders may have been similar because both samples were synthesized by the same method of alcoholic dehydration. Such powders therefore should be appropriate to use for examining the effect of aggregate on sintering behavior. Although the greatest proportion of distribution was smaller than 1 μm for the reground matrix powders, about 30% of the aggregate powder particles were larger than 2 μm. The aggregate powders thus seem appropriate for examining grain growth behavior. The XRD pattern of powders calcined at 900°C for 20 min under a nitrogen atmosphere was examined and the unique peaks of the spinel phase indicated that the complete phase formation was obtained.

Fig. 2 shows scanning electron micrographs of bodies sintered at 1200°C and 1350°C for two hours, with variations in seed amounts. The present experiment showed that matrix powders contained some aggregates that were not reground and thus caused some abnormal grain growth without the addition of aggregates. In homogeneous microstructures appeared at up to 15% seed amounts, but abnormal grain growth was suppressed above that level. At 1250°C and 1300°C, homogeneous microstructures appeared at above 10% and 5% of seed amounts, respectively. Fig. 2(d) shows SEM photograph of bodies sintered at 1350°C without the

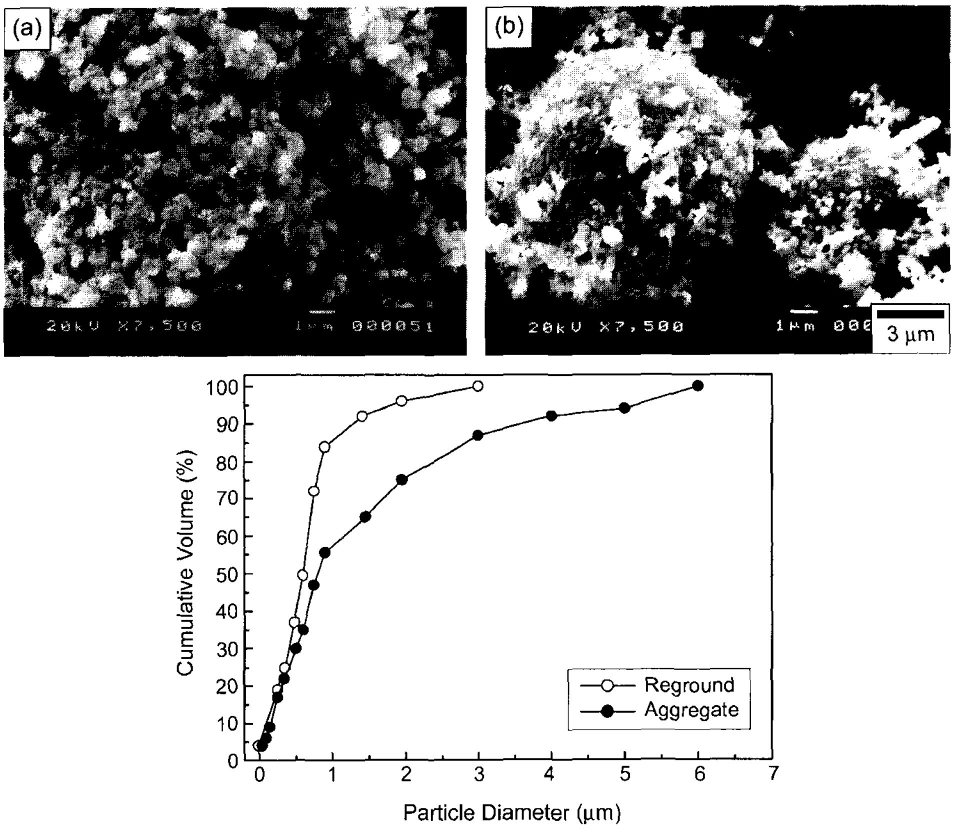

Fig. 1. SEM photographs and particle size distributions of (a) reground powders and (b) aggregates.

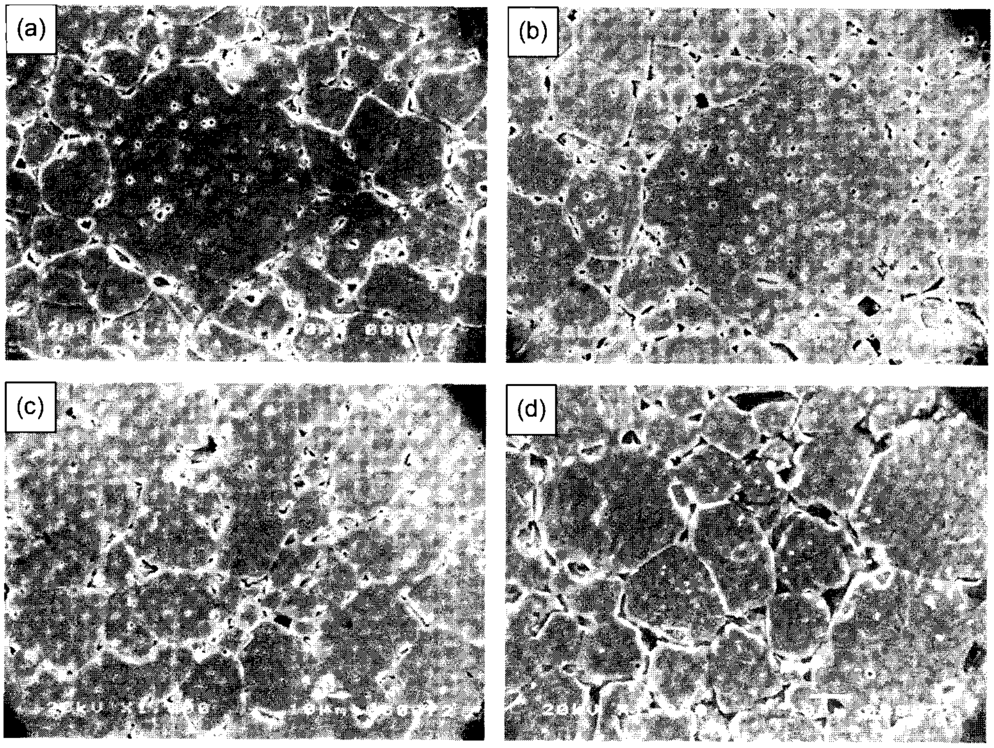

Fig. 2. SEM photographs of sintered bodies formed at 150 MPa and seed amount; (a) 0%, (b) 15%, (c) 20% sintered at 1200°C for 2 h and (d) 0% sintered at 1350°C.

addition of aggregates. As seen in that figure, abnormal grain growth was already controlled without any seeds. Compared with the others in Fig. 2, there is an increase in average grain size. Increases in sintering temperature lowered the seed amounts which abnormal grain growth could be controlled. It thus may be possible to increase the mobility behind grain growth by increasing sintering temperature. In other words, abnormal grain growth is more likely to occur with an increase in temperature.[8] Since abnormal grain growth was controlled by increasing the amount of aggregate seeds, these results confirm that aggregates can act as seeds of abnormal grain growth.

That unfractured aggregate remained in the formed body is the reason aggregates can act as seeds of abnormal grain growth. Under such conditions, nonuniformity of density can occur and this can lead to differential sintering that creates microstructure change. Fig. 3 represents changes in green density with variations in forming pressure. Increasing forming pressure caused the green densities of the pellets to increase continuously, regardless of seed amounts. An increase in the seed amount, however, caused the green density to decrease slightly because of the increased number of inner pores in the aggregates. Shin and Lee[9] calculated the density of aggregate in Mn-Zn ferrite and proposed that relative density of an aggregate made by solution technique should be about ~50%. In the Fig. 3, the green density is larger than the aggregate density above 50 MPa. Microstructural change thus is expected to occur above and below 50 MPa of forming pressure through differential sintering

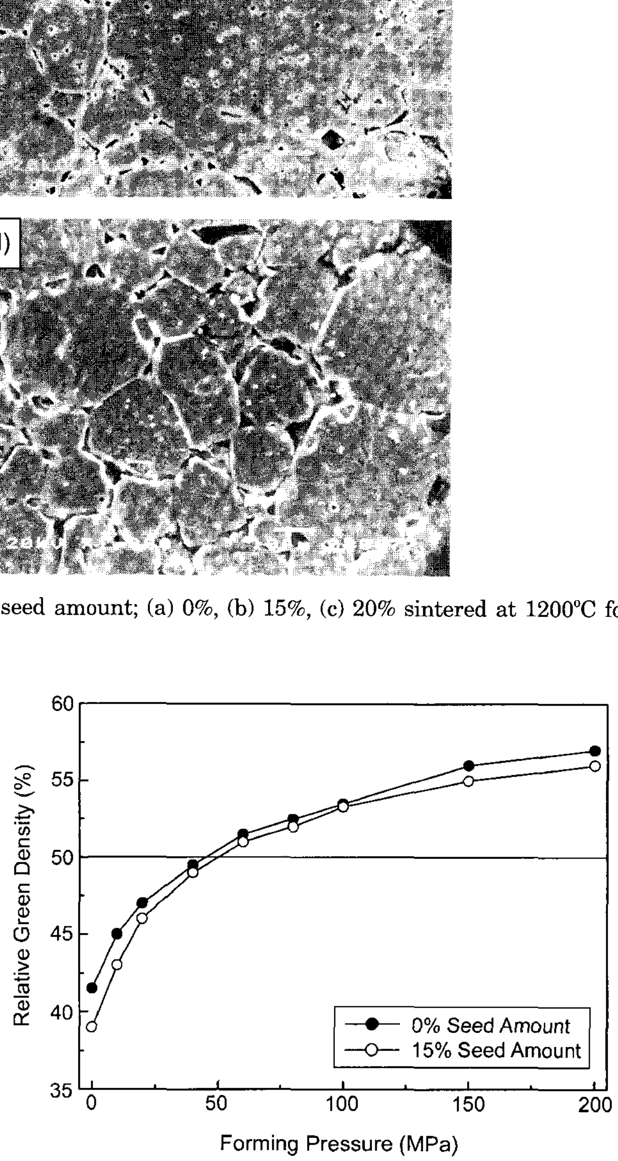

Fig. 3. Green densities with variation of forming pressure.

because of the difference in green density.

Fig. 4 shows SEM photographs of sintered bodies with seed amounts of 0% and 15% under various forming pressures. Above 100 MPa and with a seed amount of 15%, the microstructures were controlled and the seed amount of the controlled microstructure decreased with forming pressure. Because of the increase in green density with increasing forming pressure, abnormal grain growth was well controlled. These results do not accord with the assumption of Fig. 3 (i.e. that aggregates can be seeds of abnormal grain growth above 50 MPa). Compared to the green densities of

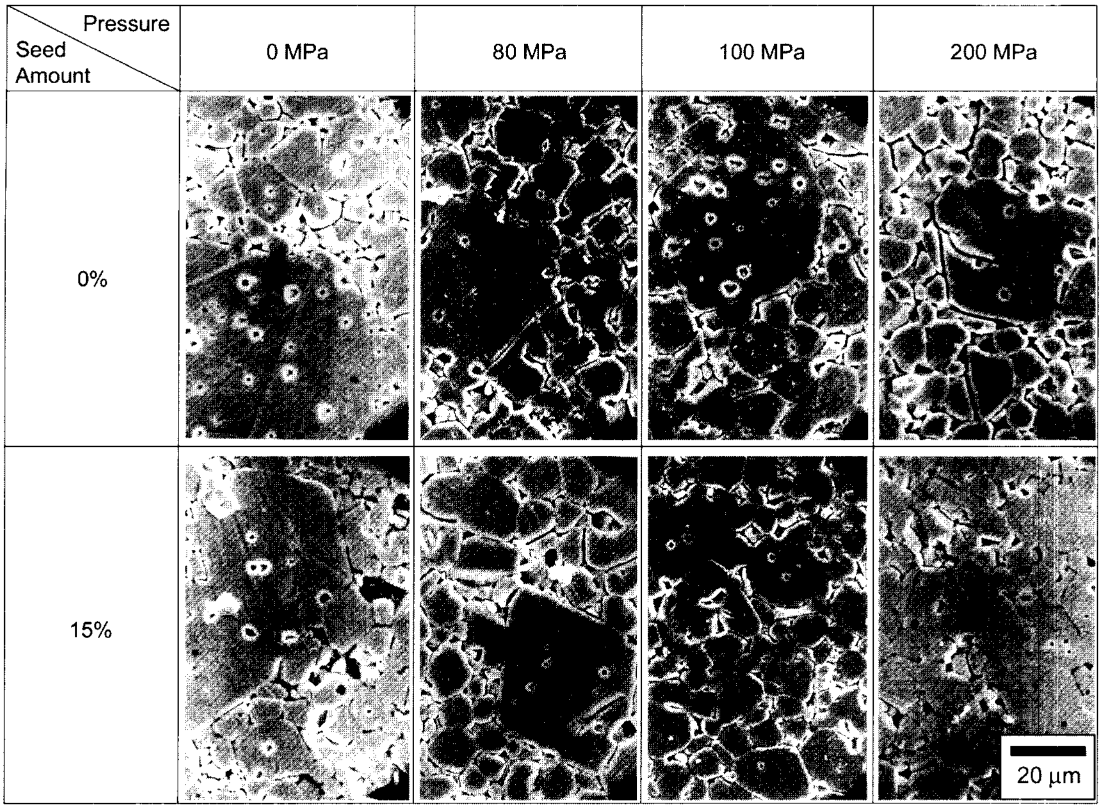

Fig. 4. Microstrcture of Mn-Zn ferrite specimens sintered at 1250°C for 2 h with variation of forming pressure and seed amounts.

Fig. 3, differences in the densities of the aggregate and the matrix are needed to effect abnormal grain growth. The aggregate may be fractured, however, by increases in forming pressure during pressing. It was proposed that the fracture pressure of an aggregate was 300 MPa.[7] The assumption that an aggregate in this pressure range (0~200 MPa) may not be fracture and can thereby act as a seed is confirmed in the present research.

4. Conclusion

Aggregates prepared by an alcoholic dehydration method are capable of acting as seeds of abnormal grain growth. As sintering temperature increases, the seed amounts to control abnormal grain growth decrease. Apparently, then, differences in green densities between the aggregate and the matrix induce the aggregate to act as a seed of abnormal grain growth.

To examine the relationship between aggregates formed during firing and the microstructure of sintered bodies, green densities were measured with variations in forming pressure. When the green density difference between the aggregate and the matrix was large, the aggregate can become the seed of abnormal grain growth. The greater the forming pressure, the more aggregates become seeds of abnormal grain growth.

REFERENCES

1. G. R. Chol, "Influence of Milled Powder Particle Size Distribution on the Microstructure and Electrical Properties of Sintered Mn-Zn Ferrite," *J. Am. Ceram. Soc.*, **54** [1] 34-9 (1970).
2. M. F. Yan and D. W. Johnson, "Impurity-induced Exaggerated Grain Growth in Mn-Zn Ferrite," *J. Am. Ceram. Soc.*, **61** [7-8] 342-49 (1978).
3. P. Sainamthip and V. R. W. Amarakoon, "Pole of Zinc Volatilization on the Microstructure Development of Mn-Zn Ferrite," *J. Am. Ceram. Soc.*, **71** [8] 644-48 (1988).
4. F. W. Dynys and J. W. Halloran, "Influence of Aggregates on Sintering," *J. Am. Ceram. Soc.*, **67** [9] 596-601 (1984).
5. W. H. Rhodes, "Agglomerate and Particle Size Effects on Sintering Yttria-stablized Zircinia," *J. Am. Ceram. Soc.*, **64** [1] 19-22 (1981).
6. F. F. Lange and M. Metcalf, "Processing-related Fracture Origins: II, Agglomerate Motion and Crack like Internal Surface Caused by Differential Sintering," *J. Am. Ceram. Soc.*, **66** [6] 398-406 (1983).
7. H. S. Shin, S. K. Lee, and B. K. Lee, "Aggregate and Necking Force in Mn-Zn Ferrite," Accepted to Materials Letters (2002).
8. J. H. Park, H. S. Shin, and B. K. Lee, "Microstructure Control of Sr-ferrite by Seed Addition," *J. Kor. Ceram. Soc.*, **32** [1] 90-4 (1995).
9. H. S. Shin and B. K. Lee, "Agglomeration Parameter, Aggregation Number and Aggregate Porosity," *J. Mater. Sci.*, **32** 4803-06 (1997).