Journal of Ceramic Processing Research. Vol. 15, No. 6, pp. 525~529 (2014)

J O U R N A L O F
Ceramic
Processing Research

Fabrication and characteristics of black alumina for LCD photo processing material

Il-Hwan Bang[a], Kun-Ok Kim[b] and Sang-Jin Lee[c,d,*]

[a]Department of Environment and Energy Engineering, Chonnam National University, Gwangju 500-757, Korea
[b]Jeonnam technopark, Jeonnam Advanced Ceramics Center, Mokpo 530-470 Korea
[c]Department of Advanced Materials Science and Engineering, Mokpo National University, Muan 534-729, Korea
[d]Research Institute of Ceramic Industry Technology, Mokpo National University, Muan 534-729, Korea

Black alumina, which has a dense microstructure, was successfully fabricated using various additives. For the application of black alumina to LCD photo device material, a low reflectivity with a dense microstructure is required as well as proper insulation resistivity. In particular, a high light absorption coefficient showing low reflectivity of below 10% is necessary for the commercial use of black alumina in photolithography. In this study, TiO_2, Fe_2O_3, and MnO_2 were used as coloring agents, and MgO and SiO_2 were used for densification through liquid phase sintering. The effects of the sintering temperature and atmosphere were investigated with the influence of additive content. MnO_2 had a strong influence on the black color of the alumina, and SiO_2 worked as an effective additive for liquid phase sintering with liquid formation by the eutectic reaction with Fe_2O_3 and Al_2O_3. The fabricated black alumina showed an 8% reflectivity and 3.94 g/cm^3 sintering density. Other properties such as flexural strength, thermal expansion coefficient, and insulation resistivity were also approached to the suitable properties of the material for chuck plate in LCD photo process.

Key words: Black alumina, Reflectivity, Microstructure, MnO_2, Liquid phase sintering.

Introduction

The photolithography is the technology that copy by making a transcription of the desired circuit design on the wafer using light, and is very important process to form the pattern designed in the manufacturing process of the semiconductor on the wafer [1]. Therefore, it is the process that the accuracy of patterning is required as a leading technology of the semiconductor miniaturization. However, because typical alumina (Al_2O_3) ceramic used in the semiconductor photo process is ivory or white color, the preciseness get lowered as the process becomes the miniature due to high reflectivity. For this reason, the black alumina material which can absorb light and has the low insulation resistance and high flexural strength is required, but yet the black alumina material is not only commercialized in the country, but also the manufacturing method of the alumina material is not established.

In the development of the ceramic color, in general, Zn-Al-Cr-Fe-based spinel-type pigment develop various colors as the ceramic pigment, the manufacturing of yellow, red and black ceramics are possible according to the content of Al^{3+}, Cr^{3+}, Fe^{3+} [2-15]. In particular, it has been reported that there is α-Al_2O_3 type solid solution which is $(Cr, Fe)_2O_3$ as the composition for the black, but $(Co,Ni)O$-$(Cr,Fe)_2O_3$-based spinel is suitable for high temperature materials, and the addition of Ti or Mn-based oxide has also been used in the development of black color [1, 2]. In addition, there is the blackening by the method that preventing the oxidation of the carbon and impregnating in the vacuum atmosphere, but because still the process has not been established, it has not been generalized [16].

In this study, in order to develop the material of the black alumina chuck plate for LCD8 generation photo process, the characteristics of the alumina ceramic was considered by adding the coloring and the sintering agents for the increase of light absorption factor in it. In particular, in the case of TiO_2 and MnO_2 which are the colored additives, because they have a bad impact on the properties of final sintered alumina depending on the additive content, the suitable optimal combination conditions for the black alumina material were derived through the experiments. The sintered density, reflectivity, color, insulation resistivity (at room temperature), flexural strength and thermal expansion coefficient of the black alumina were controlled by the change of experimental parameters so that is approached to the target making the performance indicator of TOTO Company in Japan suited for the material of the chuck plate for photo process as the aim. In particular, the experiments were conducted with a focus on the reflectivity of less than 10% and on maintaining the density of more than 98% of theoretical density.

Experimental Procedure

Manufacture of Black Alumina

Sub-micron-sized Al_2O_3 powder (Al-160SG-3, Showa

*Corresponding author:
Tel : +82-61-450-2493
Fax: +82-61-450-2498
E-mail: lee@mokpo.ac.kr

Table 1. Composition of Black Alumina for 1st Experiment (wt%).

Sample No.	Al_2O_3	TiO_2	Fe_2O_3	TiC	MgO
A1	97.0	0.5	2.0	0.3	0.2
A2	96.7	0.5	2.0	0.3	0.5
A3	96.2	0.5	2.0	0.3	1.0
A4	95.7	0.5	2.0	0.3	1.5
A5	95.5	1.0	3.0	0.3	0.2
A6	95.2	1.0	3.0	0.3	0.5
A7	94.7	1.0	3.0	0.3	1.0
A8	94.2	1.0	3.0	0.3	1.5
A9	93.7	1.0	3.0	0.3	2.0

Table 2. Composition of Black Alumina for 2nd Experiment (wt%).

Sample No.	Al_2O_3	TiO_2	Fe_2O_3	TiC	MgO	MnO_2
B1	92.2	0.5	2.0	0.3	–	5.0
B2	91.7	0.5	2.0	0.3	0.5	5.0
B3	90.7	1.0	3.0	0.3	–	5.0
B4	90.2	1.0	3.0	0.3	0.5	5.0

Denko, Japan) was used as starting material to produce the black alumina. The step that adds the coloring agent and the sintering aid was experimented gradually changing the composition based on the results of the color change of the specimens and the reflectivity measurement. In the 1st experiment, TiO_2, Fe_2O_3 and TiC were added as the coloring agent, and MgO was added as the sintering aid in order to prevent the excessive grain growth of alumina. The notation and composition of each sample are shown in Table 1. A zirconia ball was used for uniform mixing of powders, and the powders were mixed with the wet ball milling for 12 hours using distilled water as a solvent. In each mixture, the agglomeration after drying was removed, and the powders were uni-axially pressed to the specimens of constant size. In order to examine the characteristics according to the sintering temperature, the specimens were heat treated at 1500 °C, 1550 °C and 1600 °C for 2 hours, respectively. In order to investigate the influence of the sintering atmosphere, they were heat treated at the vacuum condition and the air atmosphere, respectively.

In the 2nd experiment, the typical four compositions were selected based on the results obtained from the 1st experiment, and the experiment was conducted by adding MnO_2 of 5 wt% as the coloring agent. The notation and composition of each sample are shown in Table 2. The mixing and forming method were performed in the same way as the 1st experiment. The sintering of each specimen was performed at 1600 °C for 2 hours in the air atmosphere.

In the 3rd experiment, it was tested by adding SiO_2 in order to improve the sinterability from the results obtained through the 2nd experiment, and the experiment was performed by adding TiO_2 and Fe_2O_3 in order to determine the complex effects. The detailed composition and notation of each sample are shown in Table 3.

Table 3. Composition of Black Alumina for 3rd Experiment (wt%).

Sample No.	Al_2O_3	TiO_2	Fe_2O_3	TiC	MgO	MnO_2	SiO_2
C1	93.2	0.9	2.1	0.3	0.5	–	3.0
C2	92.3	1.8	2.1	0.3	0.5	–	3.0
C3	90.2	1.8	4.2	0.3	0.5	–	3.0
C4	90.2	1.8	4.2	0.3	0.5	3.0	
C5	88.2	1.8	4.2	0.3	0.5	5.0	
C6	85.2	1.8	4.2	0.3	0.5	5.0	3.0
C7	93.2	–	–	0.3	0.5	3.0	3.0
C8	91.2	–	–	0.3	0.5	5.0	3.0

Characterization

In order to analyze the crystal phase of sintered black alumina, the sintered specimens were analyzed by X-ray diffraction analyzer (Philips, X-Pert Pro, Netherlands) under the conditions of the scan speed of 5 °/min. The reflectivity of each specimen was measured in the range of wavelength 187 ~ 3200 nm by using the spectrophotometer (U-3501, Hitachi, Japan). The density was measured by Archimedes method preparing the square specimens of the size of 10 mm × 10 mm × 10 mm. The flexural strength was measured by universal testing machine (model 4502, Instron Corp., Canton, MA, USA) as the three-point bending method, with 5 specimens at each condition. The specimens were prepared in the size of 50 mm × 4 mm × 3 mm, and were measured after grinding the surface by using SiC paper #1200. Thermal expansion coefficient was measured by using Dilatometer (DIL 402 PC, Netzsch, Germany) up to 600 °C after polishing both sides of the specimen of the square pillars. The insulation resistance was measured according to KSC IEC 60093 standard method with the sintered specimens at a certain size. As the microstructure of sintered specimens, the surface and the fracture surface were observed by using the scanning electron microscope (SEM, Hitachi S-3400N, Japan).

Results and Discussion

All sintered samples obtained from the 1st experiment showed the density of 3.9 g/cm^3 or more, more than 97% theoretical density. The change of MgO additive content had not mainly effect on the development of black color, but even the additive content of a small amount could obtain the dense sintered body. The color of all the samples showed

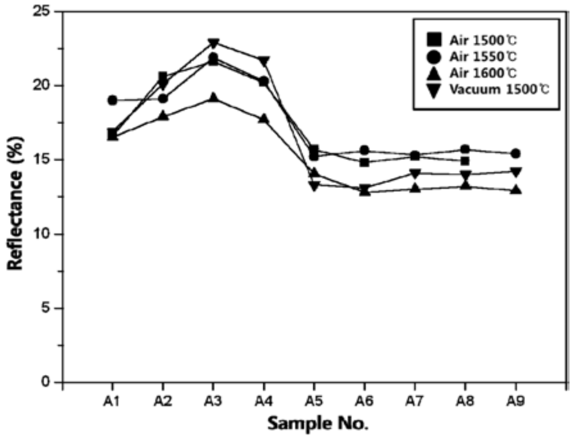

Fig. 1. Reflectivity of black-Al_2O_3 ceramics according to composition, sintering temperature and atmosphere.

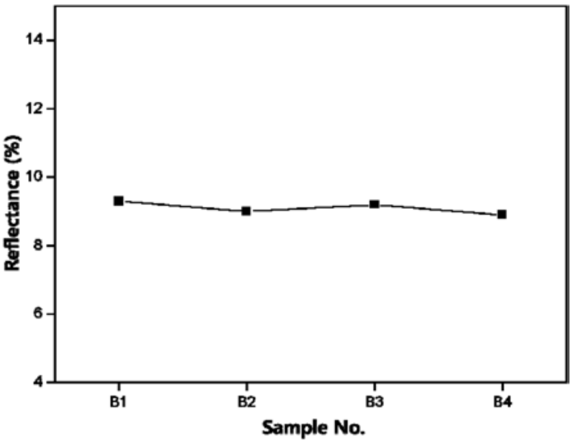

Fig. 2. Reflectivity of black-Al_2O_3 ceramics sintered at 1600 °C for 2 h according to MnO_2 addition.

gray and dark brown rather than complete black. In order to investigate the correlation according to the color development, the reflectance of each specimen was measured and the results are shown in Fig. 1. The specimens sintered in a vacuum showed higher reflectance than the sintered specimen in air up to A4, but from A5 and more specimens, the reflectance showed relatively low tendency as less than 15%. It could be found that the increase of TiO_2 and Fe_2O_3 additive content had an effect on the reduction of reflectance in a vacuum. The specimens sintered in air also showed low reflectance from A5 and more specimens, and especially, the specimens sintered at 1600 °C showed relatively the lowest reflectance. It could be found that looking at the effects of composition, the specimens which the amount of TiO_2 and Fe_2O_3 are increased showed the near color to black, and the low reflectivity was obtained. Because MgO represents the reflectivity of nearly 100%, it may be the cause that increases the reflectivity of the final specimen. Thus, the authors presented the results compensating the reflectivity allowing for the additive content of MgO added when measures the reflectivity

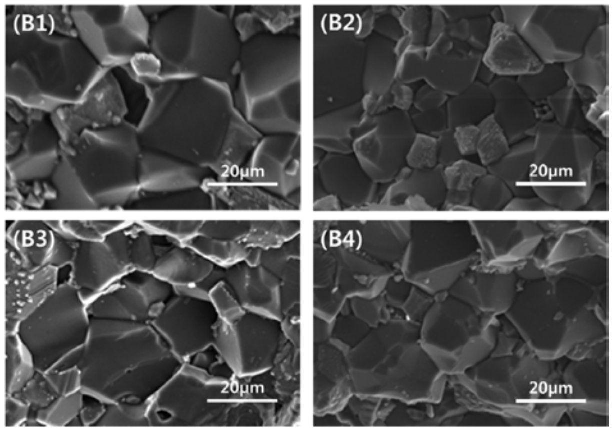

Fig. 3. SEM micrographs of black-Al_2O_3 ceramics sintered at 1600 °C for 2 h in air atmosphere according to MnO_2 addition.

in order to consider only impact of the coloring agent.

Fig. 2 shows the measurement results of the reflectivity according to the addition of MnO_2. As the results that measure the degree of black color and the reflectivity by adding MnO_2 of 5 wt% into the samples four kinds of typical compositions based on the 1st experimental result, all four specimens showed in the black color for identifying with the naked eyes, and indicated the low reflectivity of less than 10%. As the results that add MnO_2 and heat treat the specimens in air, it could be confirmed that the black color of the sintered body is more developed and the reflectivity is decreased to less than 10%, but the phenomenon that the cracks were occurred in the specimens when they were sintered, was observed. It is considered that these cracks are the problem appearing during sintering by the addition of MnO_2, and it has been reported that if MnO_2 or TiO_2 is added to Al_2O_3 more than a certain amount, the excessive grain growth is caused because the migration of the grain boundary is actively happened [17]. However, it is considered that because on the contrary, the effect of MgO on the inhibition of the grain growth during sintering of Al_2O_3 is developed, the complex action would have influenced on the sintering. Fig. 3 shows the observation results of the microstructure of the fracture surface after the sintering of the samples by the 2nd experiment. Considering that the initial powder of alumina is sub-micron size, it could check that the grain growth was actively occurred through the sintering. This can be considered as the result shown by the action of TiO_2 and MnO_2 added as the coloring agent. In particular, in the case of B1 and B3 specimens which MgO was not added, the particle size was relatively larger, and the pores were partially observed. The grain growth of the specimens which MgO was added, was relatively inhibited, and showed the microstructure that the pores were reduced. However, large and small cracks were observed in all specimens. Most of integranular fracture was observed in all specimens, and the traces

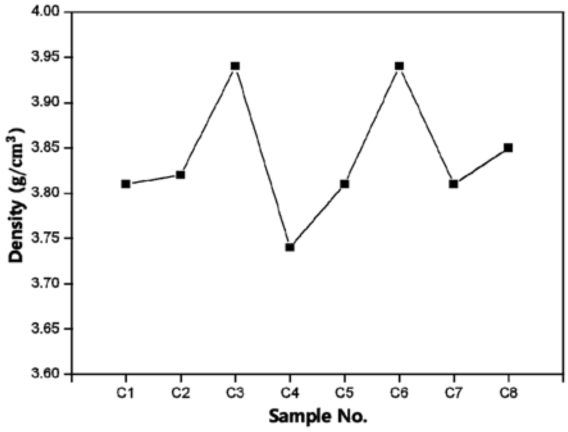

Fig. 4. Sintered density of black-Al_2O_3 ceramics sintered at 1400 °C for 2 h in air atmosphere according to SiO_2 addition.

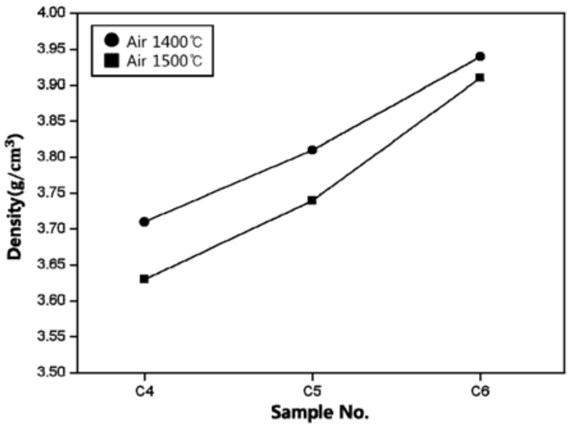

Fig. 5. Sintered density of black-Al_2O_3 ceramics (C4 ~ C6 samples) sintered at 1400 °C and 1500 °C for 2 h in air atmosphere.

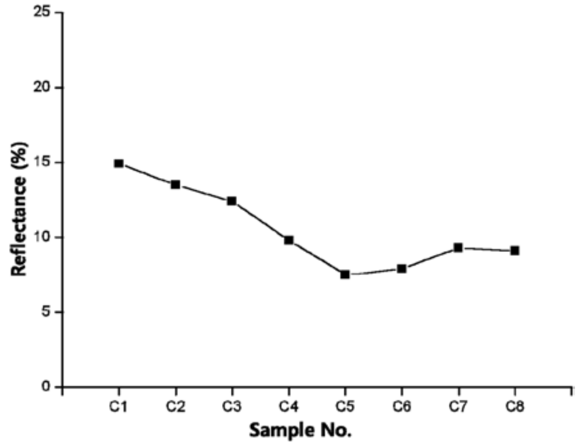

Fig. 6. Reflectivity of black-Al_2O_3 ceramics sintered at 1400 °C for 2 h in air atmosphere at each composition.

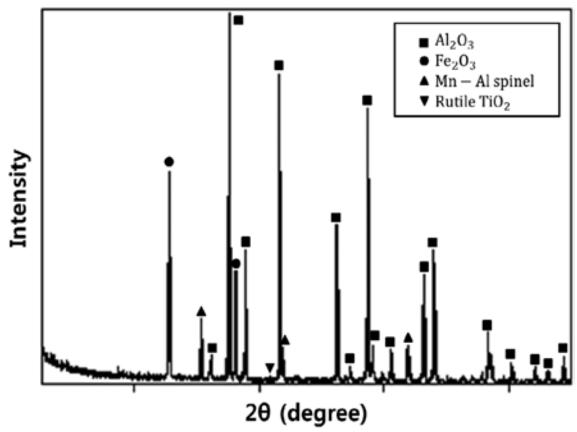

Fig. 7. XRD pattern of black-Al_2O_3 ceramic (C6 sample) sintered at 1400 °C for 2 h in air atmosphere.

of liquid could not be almost found.

As the results sintering at 1400 °C by adding of SiO_2 in the selected specimens in order to solve the problems occurred by the addition of MnO_2, the cracks were not observed in the specimens adding SiO_2, but some specimens were not developed the black color. C1 ~ C3 specimens has not been made black color, and C4 ~ C6 specimens shoot out the black color enough to identify visually. C7 and C8 samples also showed a color near to black. Fig. 4 shows the results measuring the density of each specimen. Comparing the density of C4 ~ C6 that were converted to black well, C4 showed 3.8 g/cm^3 or less, and C5 and C6 specimens showed the value of 3.8 g/cm^3 or more, respectively. The composition of C5 and C6 is the difference whether SiO_2 is added. The density of C6 specimen which SiO_2 is added is 3.94 g/cm^3, which showed higher values than C5 specimen not added SiO_2. Fig. 5 shows the changes of the density of the sintered specimens at 1400 °C and 1500 °C, respectively. In the case of the specimen sintered at 1500 °C, relatively low density values were observed. The appropriate temperature of the liquid phase sintering was found that sintering at 1400 °C is desirable through the tendency that as the temperature is increased, the density is reduced. Referring to the phase equilibrium diagram of a ternary system of Al_2O_3-Fe_2O_3-SiO_2 [18], the liquid phase is formed at low temperature by the eutectic reaction between them, consequently it could be identified that the specimen C3 and C6 represent a high density of 3.9 g/cm^3 or more. In particular, specimen C6 showed the high sintered density also at the addition of MnO_2. Fig. 6 shows the measurement results of the reflectivity, and the reflectivity of all specimens, except for the specimens of C1 ~ C3 compositions, was found exceeding the objective of this study as less than 10%. For reflectance, it is considered that the addition of MnO_2 had a large effect on blacking, but when compare the reflectivity and color of C5 ~ C8 specimens, if TiO_2, Fe_2O_3, and MnO_2 coexist, it is more effective in the blacking, so it could be identified that a lower reflectance can be obtained.

Fig. 7 shows the results of XRD analysis for the 3rd experimental specimen C6 sintered at 1400 °C The main peak was Al_2O_3, and spinel of Mn-Al system, TiO_2 and Fe_2O_3 crystalline phases were observed. In

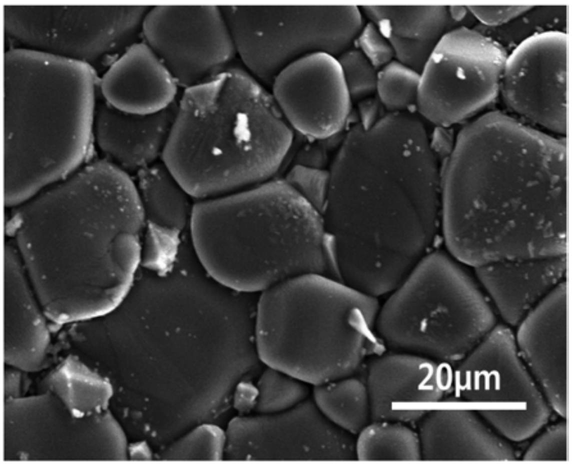

Fig. 8. SEM micrograph of black-Al_2O_3 ceramic (C6 sample) sintered at 1400 °C for 2 h in air atmosphere.

other words, it could be identified that some of the additives of the coloring agent is molten as solid solution in the alumina, and a part is made of the reactant. The average strength of specimen C6 showed 309 MPa, and the thermal expansion coefficient was measured as $5.17 \times 10^{-6}/$°C These numerical values are almost approaching values to the performance indicators of the black alumina material made in TOTO Company. If the insulation resistivity of the ceramic material for the precision chuck is less than $1 \times 10^{11}\ \Omega \cdot$cm, the damage of the substrate for FPD due to the electrostatic polarization phenomenon can be prevented, and the insulation resistivity of measured C6 specimen was measured as $2.4 \times 10^{10}\ \Omega \cdot$cm, and it could be confirmed that also the insulation resistivity of the fabricated black alumina was corresponded to the properties of matter object. Fig. 8 shows the surface microstructure after sintering of C6 specimen. The dense microstructure shown the shape that the corners are round by the development of the liquid phase sintering, was observed.

Conclusions

In this study, as the results considering the reflectivity and density of sintering alumina by adding various coloring agents and the sintering aid for manufacturing of black alumina, the following conclusion was obtained:

1) MnO_2 of various coloring agents was the most effective in the blacking, and the black alumina having the reflectivity of less than 10% was successfully fabricated by using TiO_2 and Fe_2O_3 together.

2) In the black alumina, the addition of SiO_2 was effective for densification by liquid phase sintering, and the dense sintering alumina which the sintered density is 3.94 g/cm^3 was obtained by sintering at 1400 °C for 2 hours in air atmosphere.

3) The flexural strength, insulation resistivity and thermal expansion coefficient of the fabricated black alumina are approached to the suitable properties of matter to use as the material for chuck plate in LCD photo process.

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