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Preparation of Low Density Ceramic Supporter from Coal Fly Ash

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Low density ceramic supporter was prepared by using fly ash as a starting material for the application to the biological aerated filter (BAF) system, and the effect of additives and sintering atmosphere on the apparent and bulk density of the carrier was examined. Borax, Na_2O and glass powders were added to produce liquid phase. The density of the supporter decreased as the amount of borax increased. The bulk density of 0.79 g/cm^3 and the apparent density of 1.10 g/cm^3 were obtained when the fly ash with 15% of borax was sintered at 1160℃ for 15 minutes. The density also decreased as the plate glass powders past through 212 ㎛ size were mixed. When the fly ash with 12% of glass powder was sintered at 1280℃ for 10 minutes, the bulk and apparent density were 0.90 g/cm^3 and 1.00 g/cm^3, respectively. Apparent density of 1.6 ~ 1.8 g/cm^3 was obtained when the fly ash was sintered at 1200℃ in a weak reducing atmosphere. By maintaining the reducing atmosphere and sintering at a high heating rate, the liquid phase was formed from the reduced composition of fly ash. This resulted in the formation of closed pores that enabled the low apparent density.

Introduction

In recent years, biological aerated filter (BAF) process has been more deeply recognized and applied for treating sanitary and industrial waste water instead of widely adopted conventional activated sludge process [1]. The basic principle of the BAF process consists in that waste water flows and circulates around a contacting medium whereupon microorganisms accumulate and oxidizingly decompose organic substances included in the waste water resulting in removal of the waste products.

The important design subject of the BAF process is a contacting element upon which bacterial solids accumulate. Conventionally plastic contacting element for microorganisms has been used. However, it has not yet proved to be suitable for bacteria growth because it hardly allows accumulation of bacteria due to its slippery surface. Furthermore, with thickening of the biological layer on the plastic surface, the bacteria in the inner part become to be anaerobic and a large amount of the layer may fall off from the element. On the contrary, ceramic material serves as a site where the gradual alternation of bacteria is possible in such a way that various kinds of microorganisms propagate at different rates on the ceramic surface and may take off therefrom with different senile circulation.

The BAF system can be minimized in occupying area by designing vertical biological film tank. In this case, the back-washing process to eliminate the senile microorganisms requires light weighted ceramic supporters, which enable the water stream from bottom to upward flow well without the resistance of supporters. For this purpose the low apparent density of ceramic supporters is required. In other words, many closed pores have to be formed in the supporter.

In this study, we prepared ceramic supporter for BAF process from coal fly ash, and examined the effect of flux addition on the apparent and bulk density. The heating rate effect, which is related with the sintering atmosphere, was also investigated.

Experiment

The coal fly ash wasted from power plant in Korea was used as a starting material, and the chemical composition was shown in Table 1.

Table 1 Chemical composition of coal fly ash powders (wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O
60.83	23.66	3.48	2.71	0.46	1.07
Na_2O	TiO_2	MnO	P_2O_5	F.C.	
0.50	1.00	0.04	0.56	3.5	

The fly ash powders and flux were dry mixed in a plastic vessel for 1 hour. Pellitizer was used to form the powders as ball-like pellet by adding 0.4 wt% PVA solution. 5-6 mm sized pellets were selected by sieving.

Pellets were sintered in the muffle type electric furnace. The unburned carbon was eliminated by holding the temperature at 800℃ for 2 h. Temperature was raised to sintering temperature at the heating rate of 600℃/h, and maintained for 10-20 min at each sintering temperature.

The sintering atmosphere was controlled by the heating rate. The fast heating of 1000℃/min was obtained by inserting pellets into hot zone of the tube type electric furnace from outside in a short time. Closing the inlets of the tube after inserting pellets maintained weak reducing atmosphere during sintering. The normal heating rate was 10℃/min.

The apparent and bulk density of sintered pellets were measured by Archimedes method.

$$\text{Apparent density} = \rho_w \times W_1/(W_3-W_2)$$

$$\text{Bulk density} = \rho_w \times W_1/(W_1-W_2)$$

Here, W_1, W_2 and W_3 are dry weight, suspended weight of water saturated pellet in water and water saturated weight, respectively. ρ_w is density of water.

The phase analysis and microstructure observation were done by X-ray diffractometer and scanning electron microscopy, respectively.

Results and Discussion

Properties of Fly Ash

The average particle size of coal fly ash was around 20 μm. The particle shape is shown in Fig. 1. Coal fly ash is composed of various chemicals as shown in Table 1. Therefore, it has complex sintering mechanism and a number of reactions occur during sintering. The unburned carbon contained in fly ash affects the sintering, and may alter the atmosphere in case of incomplete elimination.

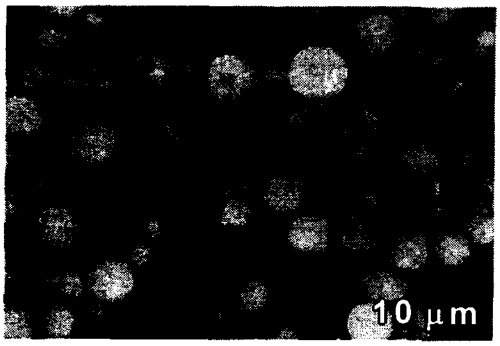


Fig. 1. SEM photograph of coal fly ash.

Fig. 2 represents the apparent and bulk density of fly ash at various sintering temperatures. The bulk density increases and apparent density decreases as the sintering temperature increases, and they finally reach to the same density at 1300℃. The close pores were formed during sintering by liquid phases originated from various impurities. These contributed to the lowering of apparent density.

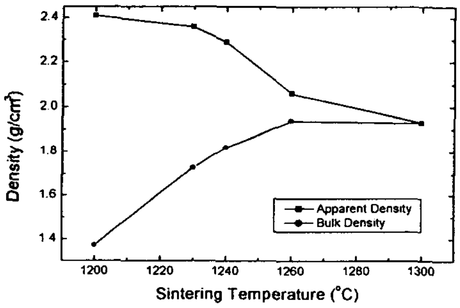


Fig. 2. The effect of sintering temperature on the apparent and bulk density.

Fig. 3 shows the microstructure of pellet sintered at 1280℃ for 10 min. Closed pores with several micrometers or over are observed, but there are few pores. Fig. 4 is XRD result of the above sample. Fly ash is composed of mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2). After sintering, it as found that anorthite phase ($(Ca,Na)(Al,Si)_2Si_2O_8$) appears.

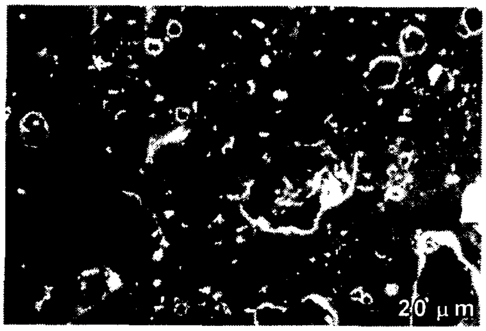


Fig. 3. SEM photograph of fly ash 1280℃ for 10 min.

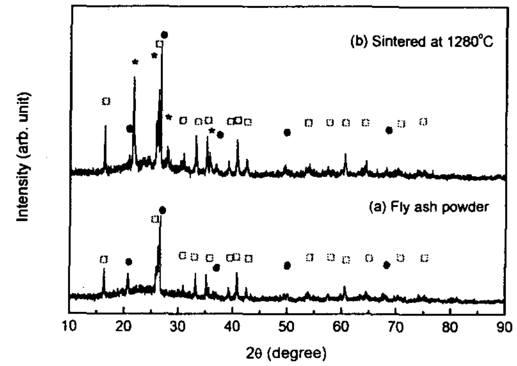


Fig. 4. X-ray diffraction patterns of fly ash. (a) Fly ash powder, and (b) sintered fly ash at 1280℃ for 10 min. The symbols □ , ● and * represent mullite, quartz and anorthite phases, respectively.

The Effect of Flux Addition

Three kinds of flux were added to fly ash, and their effect on the sintered density was examined. Fig. 5 shows the density variation according to the addition of borax ($Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$). The apparent density after sintering at 1210°C for 15 min decreases to 1.4 g/cm^3 when borax is added above 10 wt%. The lowest density was obtained at 1160℃ for the 15% of borax added pellet. At this condition, apparent density and bulk density were 1.10 g/cm^3 and 0.79 g/cm^3, respectively. The density decreases as the sintering temperature increases because sufficient amount of liquid phase is formed. However, density again increases above the temperature owing to the excessive liquid phase filling into pores [2]. Optimizing the sintering temperature and time is necessary to get low density.

Fig. 6 represents the effect of Na_2O addition on the density. The density slightly decreases as the added amount of Na_2O increases. Na_2O has property as lowering the viscosity of liquid phase. Therefore, it may be added small amount with other fluxes.

The effect of plate glass powder addition on the density is shown in Fig. 7. The chemical composition of plate glass appears in Table 2. The most part of the glass is SiO_2 with 13.80 wt% of Na_2O. It is expected that glass will react well with fly ash when glass melts. Apparent density and bulk density of 1.00 g/cm^3 and 0.90 g/cm^3, respectively, were obtained by adding 12 wt% of glass.

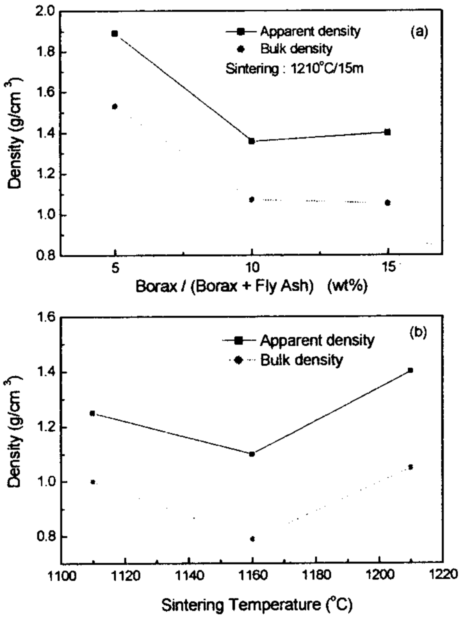


Fig. 5. (a) The effect of borax addition on the density of fly ash sintered at 1210℃ for 15 min. (b) The effect of sintering temperature on the density of fly ash. The borax was added 15 wt%.

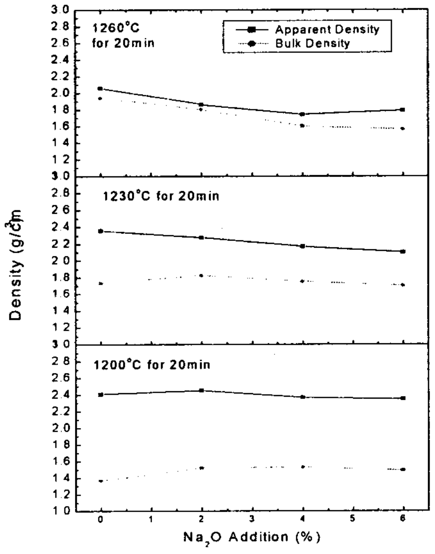


Fig. 6. The effect of Na_2O addition on the density of fly ash.

Fig. 8 represents the fractures surface of pellet sintered at 1280℃ for 10 min with 8% of glass powder. Contrary to Fig. 3, it is found that many closed pores are formed. According to the pore filling model [2], there appears a stage during sintering where the liquid phase spreads uniformly on the surface of grains. When sintering is finished at this stage, the microstructure of pellet becomes uniformly distributed closed pores. The microstructure shown in Fig. 8 was obtained by completing sintering at the liquid rearranging stage, which result in high closed pore ratio and consequently low apparent density. Fig. 9 is the X-ray diffraction pattern of the glass added pellet. The amount of anorthite phase increased and mullite decreased compared to Fig. 4(a). The reaction between fly ash and chemicals such as SiO_2, Na_2O and CaO contained in glass may have formed anorthite. The increase of background in 20-30° of diffraction angle means that the liquid phase formed during sintering does not crystallize and remains amorphous state.

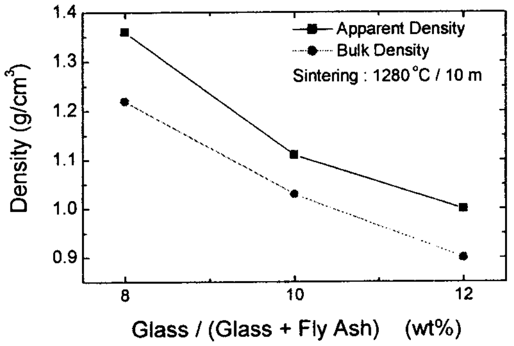


Fig. 7. The effect of plate glass addition on the density of fly ash sintered at 1280℃ for 10 min.

Table 2 Chemical composition of plate glass (wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO
70.01	1.00	0.12	9.90
MgO	K_2O	Na_2O	SO_3
3.09	0.30	13.80	0.30

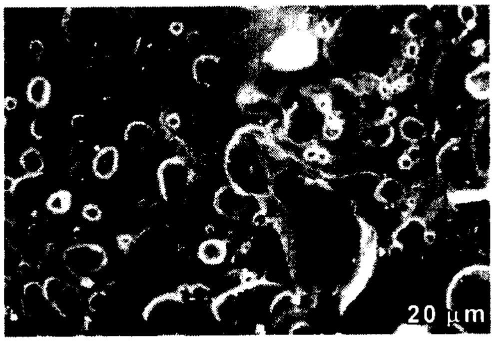


Fig. 8. SEM photograph of the fly ash sintered at 1280℃ for 10 min with the addition of glass powder.

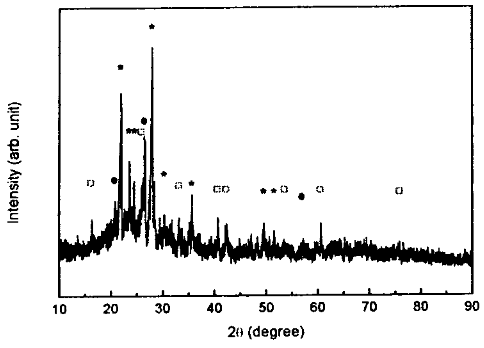


Fig. 9. X-ray diffraction patterns of fly ash sintered at 1280℃ for 10 min with the addition of glass. The symbols □ , ● and * represent mullite, quartz and anorthite phases, respectively.

The Effect of Heating Rate

Fig. 10 shows the effect of heating rate on the density. When the pellet was sintered with normal heating rate, 10℃/min, the apparent density was above 2.2 g/cm^3. On the contrary, the apparent density of fast heated pellet was as low as 1.6-1.8 g/cm^3. As mentioned in Experiment, the sintering atmosphere changes into weak reducing when the air flow inside the tube furnace is cut off because carbon of fly ash does not completely burn out. If the heating time is very short, there is not enough time to burn the carbon and consequently the atmosphere becomes more reducing. However, although the air flow is cut off, carbon is completely burned out at the normal heating rate where enough time is given.

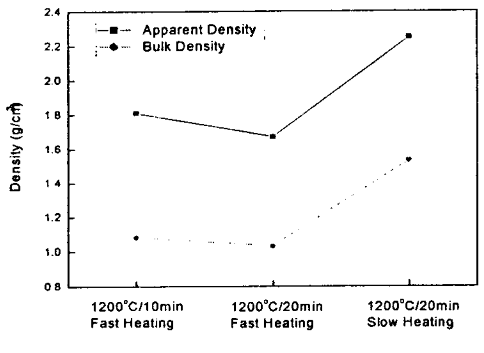


Fig. 10. The effect of heating rate on the density.

It is expected that unburned carbon will change and reduce the composition at high temperature. The phase change between slow and fast heating rate is shown in Fig. 11. The main phases of both samples are mullite and sillimanite (Al_2SiO_5). The difference is the appearance of $Fe_2Al_4Si_5O_{18}$ composition in slow heating. From this the sintering mechanism of fast heating rate can be explained as follows. Among the chemical composition of fly ash (Table 1), the most easily reducing compound is Fe_2O_3. This is reduced to FeO by the remaining carbon, and fayalite (Fe_2SiO_4) can be formed by the reaction between FeO and SiO_2. The melting point of fayalite is around 1200℃, which is much lower than that of mullite (~1850℃) and sillimanite (~1600℃) [3]. Therefore, liquid phase sintering is proceeded by the lpore filling mechanism at the sintering temperature as low as 1200℃.

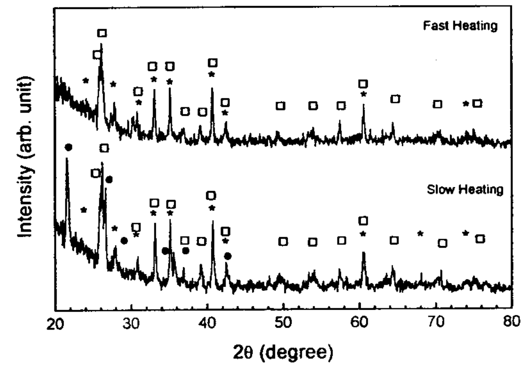
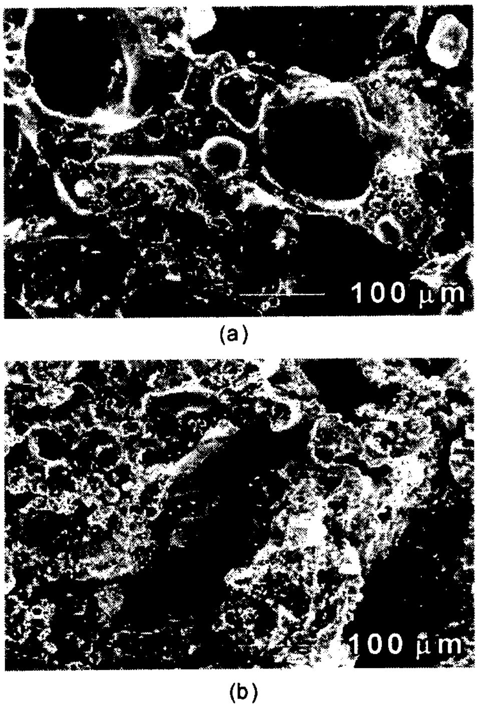


Fig. 11. X-ray diffraction patterns of fly ash sintered at a fast and slow heating rate. Symbol ● denotes the $Fe_2Al_4Si_5O_{18}$ phase, □ denotes the $Al_6Si_2O_{13}$ (mullite) phase, and * denotes the Al_2SiO_5 (sillimanite) phase, respectively.



(a)

(b)

Fig. 12. SEM photographs of the fractured surface of fly ash sintered at a fast heating rate. (a) Shell area and (b) core area of the fractured surface.

On the contrary, liquid phase is not formed when the carbon is completely burned out and therefore Fe_2O_3 is not reduced. The closed pores are not formed in this case. The unreduced Fe_2O_3 phase reacts with Al_2O_3 and SiO_2, which results into compound such as $Fe_2Al_4Si_5O_{18}$. This phase was detected by XRD because it was not formed by liquid phase reaction. However, the liquid phase formed at fast heating could not be detected by XRD due to the amorphous state.

Fig. 12 shows the microstructure of fast heated pellet. Fig. 12(a) and (b) represent the shell area and core area of the pellet, respectively. As can be seen in the figure, a number of closed pores are observed in the shell. On the contrary, pores in core area have irregular shape. The microstructure of polyphase is determined by the local equilibrium between surface tension [4]. If the dihedral angle is larger than 60°, the phase becomes isolated. The low dihedral angle enables the continuous shape along the edge of grain. Pores in (b) have low angles between grains, and it is known that these pores are connected each other, which results in open pores. On the other hand, liquid phases spread to outer surface of pellet and form closed pores. This leads to low apparent density.

Conclusion

In conclusion, low density ceramic supporter for BAF system was prepared form coal fly ash powder. It was found that, by adding some flux additives and by changing sintering atmosphere, the apparent and bulk density of the supporter could be controlled. Borax, Na_2O and glass powders were added to produce liquid phase, and keeping reducing atmosphere also formed liquid phase. The apparent density ranging 1.1 ~ 1.8 g/cm^3 was obtained by optimizing the flux composition and sintering schedule.

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