Ceramic **Processing Research**

Effect of oxide coating on artificial aggregates made of reject ash to prevent sticking phenomenon

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Homogeneously bloated aggregates formed by sintering at rising temperatures require higher temperature than aggregate bloated by the black core mechanism. Much liquid can be produced on the aggregate surfaces and induce sticking between the aggregates. In this study, highly refractory oxides, Al₂O₃ and SiO₂, were coated onto the aggregate surfaces in order to control sticking. The degree of sticking was analyzed by identifying the phases formed and measuring the neck length (2x) of two aggregates (radius = r) stuck together. As the amount of coating increases, the (x/r) ratio decreases, indicating that the degree of sticking was reduced. For the Al₂O₃ coating, a smaller particle size of the coating powder leads to a greater aggregate surface area that can be coated, which prevents sticking between the aggregates. For the SiO₂ coating, increasing the particle size of the coating powder decreased the (x/r) ratio in the $1 \sim 2$ wt% coating, while the ratio increased for coating above 3 wt% due to the lower melting temperature of amorphous silica and the generation of β -cristobalite. The proper amounts and suitable particle size of the Al₂O₃ and SiO₂ coating materials were obtained for manufacturing homogeneously bloated aggregates using 100% reject ash. These results could be used as basic data for the development of a mass-production process using a rotary kiln.

Key words: Artificial aggregates, Reject ash, Sticking phenomenon, Oxide coating, Alumina, Silica, Neck length

Introduction

Thermal power plants produce about 6.8 million tons of fly ash and 1.5 million tons of bottom ash annually in Korea [1]. The fly ash is mostly recycled, due to its fine particle size and homogeneous composition. But some larger fly ash containing high carbon content called 'reject ash' is mostly disposed of by reclamation dumping [2]. The recycling of reject ash has emerged as new concern, and many studies have been performed. One of the great advantages in fabricating artificial aggregates using reject ash is the opportunity for largescale recycling. Furthermore, highly functional properties of aggregates can be obtained for application in the environmental and construction fields [3-5].

The artificial aggregates are usually fabricated by the direct sintering method, which involves putting a sample into a preheated furnace to a specific temperature. The aggregates are bloated by the 'black core' mechanism, after which the cut cross sections of the aggregates are composed of a black core inside a redcolored shell. However, the artificial aggregates bloated by the black core mechanism often show uneven pore size distribution. Moreover, if the black core part develops excessively such that it penetrates the surface, cracks are generated in the surface, resulting in irregularly-shaped aggregates that have poorer mechanical properties [6-8].

Kang et al. reported that aggregates fabricated using reject ash by the temperature-raising sintering method showed excellent bloating behavior with uniform microstructure and no black core phenomenon [9]. These aggregates are denoted as 'homogeneously bloated aggregates'. However, the homogeneously bloated aggregates made by temperature-raising sintering require higher temperature than aggregate bloated by the black core mechanism. Therefore, much liquid could be produced on the specimen surface, which induces sticking between the aggregates. The sticking phenomenon can clog up the rotary kiln and make a lump of aggregate, which makes mass production difficult. Therefore, addressing sticking problems is crucial for the mass production of artificial aggregates, especially for compositions in which a large amount of liquid is generated during sintering.

In this study, the conditions to control the sticking phenomenon between aggregates were examined in the fabrication of homogeneously bloated aggregates using 100% reject ash by the temperature-raising method. The coating of amorphous SiO₂ and crystalline Al₂O₃ powders on the surface of the aggregate was attempted before the sintering process. The degree of sticking was analyzed by identifying the phases formed and measuring the neck length of two aggregates stuck together.

Experimental Procedures

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The coal reject ash used in this study was obtained from 'Y' power plants in Korea. The percent com-

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Frame oxide	Neutral oxides		Fluxing oxides					Others			
SiO_2	Al_2O_3	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P_2O_5	С	Ig. loss
60.1	19.1	3.0	1.1	0.5	0.3	0.5	0	1.0	0.4	9.1	4.9

 Table 1. Chemical composition of as-received coal reject ash (wt%).

position of the reject ash analyzed by XRF is shown in Table 1. The reject ash contained 9.1% unburned carbon. The surface of unburned carbon is hydrophobic, so a raw material containing much amount of unburned carbon is difficult to form using the water. Therefore, PVA 1% solution was added to improve the forming ability of the reject to fabricate the spherical shape of green body of 10 ± 1 mm diameter.

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The amorphous SiO₂ and crystalline Al₂O₃ powders were selected as coating materials for the surface of green aggregates. The amount of coating materials varied from 1 to 12 wt%, and 4 particle sizes of each coating material were used $(38 \,\mu\text{m}^2, 38 \sim 45 \,\mu\text{m}, 45 \sim 90 \,\mu\text{m}$ and 90 μm^+). The coating was done by putting the green aggregate with coating materials into a 50-cc cylindrical plastic container and rotating it at 140 RPM for 10 min.

The coated aggregates were dried at 110 °C for 24 hrs, and sintered by the temperature-raising method, in which the green body was put into the furnace preheated at 800 °C. The temperature of the furnace was raised with a heating rate of 15 °C/min up to 1275 °C and held for 15 min. Then, the aggregate was cooled to room temperature by discharging them immediately after sintering.

The identification of crystal phases of the sintered body was analyzed by XRD (X-ray Diffractometry; D/ MAX-C, Rigaku Co.). Images of the artificial aggregates were observed and the neck length of two aggregates stuck together was measured using an optical microscope (DCS-105, Sometech Vision, Korea).

Result and discussion

The composition of the reject ash is shown in Table 1. In order to predict the possibility of bloating for the raw materials, the composition oxides were classified based on the traditional three-axis system, representing the structural oxide, fluxing oxide, and neutral oxide. The reject ash contained 9.1 wt% unburned carbon, which is too much to fabricate an aggregate. In general sintering processes, the excessive carbon should be



Fig. 1. Ternary diagram of SiO₂-Al₂O₃-flux ceramic system. The area surround by dotted line represents the bloating zones during sintering process presented by Riley [8].



Fig. 2. The crystal phases identified by XRD of as-received and calcined coal reject ashes (R/A), and two coating materials, SiO_2 and Al_2O_3 powders.

removed, because it emits much gas by oxidation. However, Kang and et al. could manufacture homogeneously bloated aggregates using as-received reject ash without any calcination [9]. In Fig. 1, the area surrounded by the dotted line indicates the bloating zone reported by Riley [10]. According to Riley's study, the most important factors for the bloating of ceramics are the sintering temperature and chemical composition. When the green body is heated, a viscous liquid phase is formed to capture gases generated inside of the specimen which cause the aggregates to be bloated [8]. Because the reject ash (•) deviates from the bloating area defined by Riley, bloating using the normal sintering method is difficult. So, the homogeneously bloated aggregates were made by the temperatureraising sintering method reported by Kang et al. [9].

The amorphous SiO_2 and crystalline Al_2O_3 powders were selected as the coating materials. The XRD results for the SiO_2 , Al_2O_3 , as-received reject ash, and calcined reject ash are shown in Fig. 2. The Al_2O_3



Fig. 3. The formation of crystal phases for the sintered body containing reject ash and Al_2O_3 powders identified by XRD. The weight ratio of reject ash and Al_2O_3 powders is 1 : 1 and the sintering was performed at 1275 °C for 15 min.



Fig. 4. The XRD results showing the effect of particle size of SiO_2 powders on the formation of crystal phases for the sintered body containing reject ash and SiO_2 powders. The weight ratio of reject ash and SiO_2 powders is 1 : 1 and the sintering was performed at 1275 °C for 15 min.

powder has high-intensity peaks showing well-grown crystal, while SiO_2 is in an amorphous state. The asreceived reject ash was composed of quartz and mullite crystal phases. But, most of the quartz phase disappeared, and the peaks for mullite phase were reduced after calcination.

The reacting behavior between the reject ash and coating material at high-temperature was analyzed. The XRD analysis on the specimens containing reject ash and coating material (1 : 1 by weight) sintered at 1275 °C for 15 min are shown in Fig. 3 and Fig. 4. In the sintered body containing reject ash and Al_2O_3 , the major phase was Al_2O_3 , and the secondary phase was mullite (Fig. 3). The crystal peak of Al_2O_3 phase in the coating powder was reduced to 50%, due to the reaction of alumina with the quartz in the reject ash generating the mullite ($3Al_2O_3 \cdot 2SiO_2$), as shown in Fig. 2. The change in particle size of the alumina did not affect the peak intensity in XRD.

In the reaction between SiO_2 and reject ash, β cristobalite as the major phase and mullite as the secondary phase were formed, as shown in Fig. 4. As the particle size of the coating material decreased, the

Table 2. The (x/r) ratio* between two aggregates made of reject ash as a function of amount of coating material and its size.

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Coating Materials	Amount Size	1 wt%	2 wt%	3 wt%	4 wt%	8 wt%	12 wt%
$ \begin{array}{c} Al_{2}O_{3} \\ \hline 38 \sim 45 \ \mu m & 0.28 \\ \hline 45 \sim 90 \ \mu m & 0.30 \\ \hline 90 \ \mu m^{+} \\ \hline 0.36 \\ \hline 0.29 \\ \hline 0.8 $	Al ₂ O ₃	38 μm ⁻	0.27	0.21	NoS**	NoS	NoS	NoS
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$38\sim 45~\mu m$	0.28	0.24	NoS	NoS	NoS	NoS
$SiO_{2} = \frac{90 \ \mu m^{+}}{45 \ \sim 90 \ \mu m} = \frac{0.48}{1000} = \frac{0.29}{0.29} = \frac{0.29}{0.29} = \frac{0.8}{0.20} = \frac{0.28}{0.27} = \frac{0.8}{0.000} = \frac{0.28}{0.200} = $		$45\sim90\;\mu m$	0.30	0.29	NoS	NoS	NoS	NoS
$SiO_{2} \frac{38 \mu\text{m}^{-} 0.48 0.40 0.28 0.27 \text{NoS} \text{NoS}}{45 \sim 90 \mu\text{m}} \underbrace{0.43 0.33 0.31 \text{NoS} \text{NoS}}_{0.28 0.26 \text{NoS}}$		90 μ m ⁺	0.36	0.29	0.29	NoS	NoS	NoS
SiO ₂ $\frac{38 \sim 45 \ \mu m \ 0.43 \ 0.33 \ 0.31 \ \text{NoS} \ \text{NoS}}{45 \sim 90 \ \mu m} \xrightarrow{\text{No experiment} ***} \frac{0.28 \ 0.26 \ \text{NoS}}{45 \sim 0.26 \ \text{NoS}}$	SiO ₂	38 μm ⁻	0.48	0.40	0.28	0.27	NoS	NoS
$\frac{45 \sim 90 \ \mu m}{1000}$ No experiment*** $\frac{0.28 \ 0.26 \ NoS}{10000 \ 0.26 \ 0.26}$		$38\sim 45~\mu m$	0.43	0.33	0.31	NoS	NoS	NoS
		$45\sim90\;\mu m$	No	morim	ont***	0.28	0.26	NoS
90 μm ⁺ 0.3 0.28 NoS		$90 \ \mu m^+$	INO C2	xperim	ent	0.3	0.28	NoS

*The (r/x) ratio was measured from the pictures obtained by optical microscope as shown in Fig. 5.

**NoS indicates that no sticking between aggregates was occurred.

***No experiment was done because those conditions definitely should cause the fusion between the aggregates.



Fig. 5. The schematic diagram of neck formation between two spherical aggregates by fusion, where r = radius of aggregate and x = half length of the neck.

XRD peak intensity for the phases generated increased. The β -cristobalite phase that formed presumably originated from the amorphous SiO₂, or quartz in the reject ash. Considering the transformation temperature of 1470 °C for quartz to β -cristobalite [10], the possibility of quartz transforming into β -cristobalite in the reject ash is quite low at 1275 °C the sintering temperature. Another support for this explanation can be seen in Fig. 2, in which the quartz just disappeared, and did not transform into the β -cristobalite crystal.

The generation of the β -cristobalite crystal phase was increased with decreasing particle size of the coating material, due to the higher specific surface area, which offers many sites for nucleation. To investigate the degree of sticking among aggregates, the (x/r) ratio was introduced, where r is the radius of the aggregate and x is half the length of the neck between aggregates (Table 2). The two green aggregates were in light contact, and sintered as shown in Fig. 5. As the degree of sticking increases, the (x/r) ratio would increase. The reason for dividing x by r is to remove the effects caused by small size difference between aggregates. As seen in Table 2, to prevent sticking between the aggregate, a greater



Fig. 6. The (x/r) ratio measured in the neck between two aggregates coated with Al_2O_3 of various particle sizes. The dotted line indicates the high possibility for producing a lump of aggregates due to excessive formation of liquid during the sintering process.



Fig. 7. The effect of particle size of coating powder, Al_2O_3 on the sticking phenomenon between two aggregates showing that the amount of liquid formed in the neck increases with particle size of Al_2O_3 . (The amount of Al_2O_3 coating = 1 wt%)

amount of silica coating is required compared to alumina coating. The abbreviation NoS indicates that no sticking between two aggregates occurred.

As the amount of coating increased, the (x/r) ratio decreased, indicating that the degree of sticking was reduced. Also, the Al_2O_3 coating was more effective for preventing sticking than the SiO₂ coating. SiO₂ coating with large particle sizes of $45 \sim 90 \,\mu\text{m}$ and $90 \,\mu\text{m}^+$ was not performed, because severe sticking would be certain under these conditions. The data in the Table 2 is shown as a graph in Fig. 6 (alumina coating) and Fig. 9 (silica coating).

As shown in Fig. 6, the (x/r) ratio increased with increasing particle size of the Al_2O_3 coating powder. For the same amount of coating, smaller particle size of the coating power, led to greater coated surface area of the aggregates, which prevented sticking between the aggregates. This phenomenon can be observed in Fig. 7. The amount of Al_2O_3 coating above 3 wt%, regardless of the particle size, can prevent sticking, except with a coating particle size of 90 μ m⁺. When increasing the amount of Al_2O_3 coating, the (x/r) ratio decreases, because more aggregate surface can be shielded. This effect can be observed in Fig. 8. As the amount of Al_2O_3 coating added increased, the neck length at the



Fig. 8. The sticking phenomenon between two aggregates coated with Al_2O_3 showing that the amount of liquid formed in the neck decreases with amount of coating material. (The particle size of $Al_2O_3 = 90 \ \mu\text{m}^+$)



Fig. 9. The (x/r) ratio measured in the neck between two aggregates coated with SiO₂ of various particle sizes. The dotted line indicates the high possibility for sticking producing a lump of aggregates due to excessive formation of liquid during the sintering process.

aggregate contact was reduced.

When the (x/r) ratio is over 0.28, as indicated by the dotted line in Fig. 6, the liquid formed was overflowing the coating layer. This phenomenon can be observed by the naked eye. In this case, the sticking is serious between the aggregate, such that a giant lump of aggregates could be generated instantly in a mass-production process. The most condition for Al₂O₃ coating had an (x/r) ratio of < 0.29, except for a few conditions. The variation of the (x/r) ratio cannot be explained by the intensity or kind of crystal phases formed, because there was nearly no change to the crystal phases generated in the reaction between the reject ash and Al₂O₃ with varying particle size of Al₂O₃ (Fig. 3).

The sketched graph for the SiO₂ coating effect on the (x/r) ratio is shown in Fig. 9. The effect of the amount of coating on the prevention of sticking is similar to the case of Al₂O₃ coating; the (x/r) ratio decreased with the amount of coating. The (x/r) ratio changes with the particle size of the SiO₂ coating powder, but different tendencies were shown compared to Al₂O₃ coating, depending on the amount of coating. Increasing the particle size of the coating powder decreased the (x/r) ratio in the $1 \sim 2$ wt% coating, whereas the ratio increased for coating above 3 wt%.

The melting point of the alumina crystal is 2054 °C, while the silica has a lower melting point of 1726 °C. Furthermore, amorphous silica can be melted at a much



Fig. 10. The sticking phenomenon between two aggregates coated with 1 wt% SiO₂. The particle size of SiO₂= 38 μ m⁻. More liquid was formed in the neck compared to the Al₂O₃ coating with the same conditions, as shown in Fig. 7(a).



(b) coated with Al₂O₃

Fig. 11. Optical micrographs of cut cross section for the aggregates coated with various coating conditions.

lower temperature than SiO₂ crystal. Therefore, even though the particle size was increased, the amorphous silica was easily softened and melted in comparison with the alumina crystal, enabling the coverage of the aggregate surface. In addition, as shown in Fig. 4, the relatively smaller particle size of 38 μ m⁻ and 38 ~ 45 μ m generated more β -cristobalite phase in comparison with higher particle sizes of 45-90 μ m and 90 μ m⁺.

It is clear that the β -cristobalite crystal phase is more effective for preventing sticking between aggregates compared to amorphous silica. For the same amount of coating and size of the coating powder, the SiO₂ generated more liquid to increase the (x/r) ratio and intensify the sticking phenomenon compared to the Al₂O₃ coating. This difference can be observed by comparing Fig. 7(a) and Fig. 10.

From the (x/r) ratio data on the Al₂O₃ and SiO₂ coating in Fig. 6 and Fig. 9, the Al₂O₃ coating was verified as more effective to prevent the sticking between aggregates than the SiO₂ coating. The micro-

structure for the cross section of the artificial aggregate manufactured can be observed in Fig. 11. Most of aggregates fabricated in this study showed very similar microstructure, regardless of the kind and size of particles of the coating material. Although the black core phenomenon did not appear in the aggregate, all aggregates were well bloated with uniform microstructure and pore size distribution. Also, the microstructure showed in Fig. 11 is very similar to that in Kang's study [9].

In this study, the Al_2O_3 coating was proven to be more suitable than SiO_2 coating to prevent sticking between the artificial aggregate in large-scale manufacture processes. In conclusion, the proper amount and suitable particle size of the Al_2O_3 and SiO_2 coating materials were investigated in the manufacture of homogeneously bloated aggregates using 100% reject ash. The results obtained in this study could be used as basic data for mass-production processes using a rotary kiln.

Conclusion

The conditions to control sticking between aggregates were examined in fabricating homogeneously bloated aggregates using 100% reject ash by the temperatureraising method. For this purpose, the coating of amorphous SiO₂ and crystalline Al₂O₃ powders onto the surface of the aggregate was attempted before the sintering process. The as-received reject ash was composed of quartz and mullite. However, most of the quartz disappeared, and the peaks for the mullite phase were reduced after calcination. In the reaction between reject ash and Al₂O₃, the Al₂O₃ as a major phase and the mullite as a secondary phase were formed. The crystal peak of Al₂O₃ phase in the coating powder was reduced to 50% due to reaction with the quartz in the reject ash generating mullite. In the reaction between SiO_2 and reject ash, β -cristobalite as the major phase and mullite as the secondary phase were formed. As the particle size of the coating material decreased, the XRD peak intensity for the phases generated increased. The β -cristobalite phase formed originated from the amorphous SiO₂.

As the amount of coating increases, the (x/r) ratio decreases, indicating that the degree of sticking was reduced. For the Al₂O₃ coating, smaller particle size of the coating power led to greater surface area of the aggregates being coated, thus preventing sticking between aggregates. For the SiO₂ coating, increasing the particle size of coating powder decreased the (x/r) ratio in the $1 \sim 2$ wt% coating, while it increased the ratio in coating above 3 wt% due to the lower melting temperature of amorphous silica and generation of β cristobalite. For the homogeneously bloated aggregates using 100% reject ash, the minimum amounts of coating were 3 wt% and 8wt% for Al₂O₃ and SiO₂ coating, respectively. The Al₂O₃ coating was verified as more effective for preventing the sticking between aggregates than the SiO_2 coating. These results could be used as basic data for the development of mass-production processes for aggregates using 100% reject ash in rotary kilns.

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