Effective infiltration with polyethyleneimine-grafted colloidal alumina particles for silica-based ceramic cores

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Amine-functionalized alumina colloidal particles were prepared using polyethyleneimine (PEI) for enhancing the infiltration process of silica based ceramic core. The surface properties of PEI-grafted alumina particles were adjusted to improve their dispersion behavior in aqueous suspension, and the surface charge was adjusted to enhance their adsorption behavior, in neutral pH atmosphere, via an electrostatic repulsion force with a fused silica matrix containing an implied strong negative charge. The characteristics of the surface-modified particles were optimized as shown by the C–H stretching vibration and N–H bending vibration from FT-IR spectra, and the surface charge alternated from −3 to 45 mV. As a result, the dispersion behavior in aqueous solvent was advanced as indicated by the decrease of the polydispersity index, decrease of the average size from 178 to 130 nm, and sharpness of the particle size distribution parabola. These improvements greatly contributed to the acceleration of the infiltration time and efficiency (up to 30 min). Consequently, the promptly infiltrated specimens improved the flexural strength from 3.2 to 10.2 MPa and reduced the linear shrinkage rate from 1.91 to 1.05% as well.

Key-words : Amine-functionalization, Colloidal alumina, Fused silica, Ceramic core, Infiltration

1. Introduction

Complex structured ceramic cores, produced by injection molding, have been extensively used to produce internal cooling passages in hollow gas turbine blades and vanes. The casting process for building complex shaped bodies, such as injection, transfer, and rapid prototype printing runs, is conducted at high temperature, that is, over 1000°C, and the specimens undergo thermal stress. For this reason, all of the ingredients need to have high thermal shock resistivity and adequate flexural strength to be used for ceramic core production. Thereby, a mixture of ceramic powders consisting of fused silica (SiO₂) and zircon (ZrSiO₄) are considered to be a viable candidate material group because of their excellent high temperature properties, such as thermal shock resistance and chemical inertness, against molten metal.

Fused silica is mainly used as the matrix of a structure because it possesses a low thermal expansion coefficient (0.55 × 10⁻⁶ K⁻¹) between 25 and 1000°C) and excellent chemical resistance with molten metal. However, its structure suffers phase transformation from silica to cristobalite at a high sintering temperature (over 1300°C). This transformation of the crystal structure (β to α phase) causes shrinkage and microcracking of the ceramic core. In addition, microcracks formed by volume contraction of cristobalite decrease the flexural strength.

In our previous study, colloidal silica was infiltrated in the ceramic core of silica-zircon composite to prevent the crystallization of cristobalite. Through the adsorption of infiltrated alumina onto the surface of silica, mullite, which inhibits the formation of microcracks induced by the phase transformation of cristobalite, was formed and improved the mechanical properties. The infiltrated alumina content of the pre-sintered specimen was up to 2.54% for 150 min of infiltration time, and the flexural strength was also enhanced up to 10 MPa with the increase of the alumina content. However, the commercially available colloidal alumina suspension that was used exhibited a low zeta potential (−3 mV) in neutral pH. Therefore, the composition of the pH atmosphere, in that case pH 3.4, with the positive charge opposite to the high negative charge of the fused silica, is necessary. This is a serious disadvantage in the mass production process, because the pH is easily changed even with minor changes in the manufacturing environment.

In present study, polyethyleneimine (PEI) grafted alumina particle was prepared to enhance the infiltration process to improve the mechanical properties of the ceramic core. By functionalizing the amine group on the surface of alumina particles with PEI, the infiltration process adaptability is expected to improve with the implementation of maximum surface charge difference between alumina and fused silica in neutral pH. In addition, as the dispersion of the colloidal alumina suspension is enhanced by the strong positive charge on its surface, the improvement of the dispersion behavior of the nano-alumina particles in the aqueous solvent can be predicted. Therefore, the infiltration efficiency will be improved by improving the mobility of the particles flowing into the silica’s pore, as well.

2. Experimental process

Porous silica-based specimens for alumina infiltration were fabricated using the ceramic injection molding method. The feedstocks were composed of 64 wt% of fused silica (amorphous SiO₂, 325 mesh, >99.7%, Imerys, United States), 21 wt% of zircon (ZrSiO₄, 1 µm, 99.5%, Cenotec, Korea), and 15 wt% of...
thermoplastic mixture binder which included paraffin wax (Nippon-seiro, Japan), microcrystalline wax (Nippon-Seiro, Japan), stearic acid (C17H35O2, Samchun Pure Chemical, Korea), and oleic acid (C18H34O2, 97%, Samchun Pure Chemical, Korea). The prepared oxide powders, that is, fused silica and zircon flour, were mixed with 6-mm radius zirconia milling balls as a milling media in a polyethylene container for 48 h at 200 RPM in a ball mill machine. The mixed powder and thermoplastic binders were blended to produce the feedstocks at 80°C for 6 h under vacuum condition.

The green bodies, formed with dimensions of 6 mm × 8 mm × 90 mm based on ASTM C1161-13, were injection molded using a C-frame ceramic injection molding machine (CTM-Cl-CF-35-100HT, Cleveland Tools and Machines, United States). The conditions of the injection process were the following: temperature of 80°C, flow rate of 400 cc/s, and injection pressure of 60 bar. The thermoplastic binders were burnt out with a slow heating step (0.2 K/min), and as a pre-sintering stage, the specimens were thermally treated at 1100°C for 2 h with a heating rate of 5 K/min using a box furnace (UAF-15-27-LHE, Lenton, United Kingdom). The apparent porosity and linear shrinkage of the pre-sintered specimens were 30.1 and 0.6%, respectively.

The reagents used for the preparation of amine-functionalized alumina for infiltrating into the pre-sintered specimen were commercially available nano-sized aluminum oxide (Al2O3, APS 40–50 nm, 99.5%, Alfa-Aesar, United States) and hyperbranched polyethyleneimine (PEI, Mw 60,000, Sigma-Aldrich, United States). Five grams of alumina particles was suspended in 500 ml of deionized water and mixed with a mechanical stirrer at 400 RPM at room temperature for 1 h. Various concentrations of PEI in deionized water were administered over time into the alumina suspension and continuously mixed at 400 RPM at 80°C for 3 h. Then, the reacted particles were separated using centrifugation at 10,000 RPM for 1 h. These nanoparticles were washed several times with deionized water and collected.

The prepared pre-sintered specimens were dried into 20 wt % of the surface modified alumina powders in deionized water for up to 60 min under vacuum condition. The infiltrated specimens were dried at 110°C for 12 h. Then, the parched specimens were ultimately sintered at 1300°C for 2 h.

Fourier transform infrared spectroscopy (FT-IR, IRAffinity-1S, Shimadzu, Japan) was used to investigate the surface modified alumina particles to ensure formation of the surface functional group. To determine the degree of dispersion and surface charge alteration, the zeta-potential values, particle size distribution (PSD), and polydispersity index (PDI) were measured using dynamic light scattering (DLS) (Zetasizer Nano ZSP, Malvern, United States). The infiltrated specimens were investigated using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) and EDX mapping (Link Pentafet, Oxford Instruments, United Kingdom) to identify the microstructures and infiltration behavior, respectively. Additionally, the weight loss of the dried colloidal alumina was measured using a thermogravimetric/differential thermal analyzer (TG/DTA, SDT 2960 Simultaneous, TA instruments, United States). The phase transformation from fused silica to cristobalite, residual alumina, and mullite in the sintered specimens were analyzed using a X-ray diffractometer (XRD, D/Max-220, Rigaku, Japan) under Cu Kα radiation (λ = 1.54178 Å). The mechanical properties, such as the flexural strength and shrinkage rate, were measured using the 3-point bending test in a span size of 80 mm and crosshead speed of 1.0 mm/min with a universal testing machine (UTM, H105K, Hounsfield, United Kingdom).

3. Results and discussion

The surface functional groups of modified alumina particles with different amounts of PEI were identified from FT-IR spectra. The characteristic absorption band of the Al-O stretching vibration was observed at 575 and 787 cm⁻¹, and the broad absorption peaks in the range 3700–3000 cm⁻¹ were attributed to the hydroxyl group (Al-OH) in all specimens, as shown in Fig. 1.12,13 In the PEI treated spectra, however, additional specific peaks were revealed at 2830, 2950, and 1630 cm⁻¹, and these were assigned, respectively, to the C–H stretching vibration and N–H bending vibration, which was evidence of functionalization with the amine group.14 The width and depth of the absorption band between 3700–3000 cm⁻¹ in the PEI-grafted alumina particles were slightly larger than those of the as-received alumina particles. This was probably due to the overlapping of the stretching vibrations of –OH and N–H.15 Increasing amount of PEI, the depths of the –OH, C–H, and N–H vibrations gradually deepened until a composition of 5 wt % was reached. It was inferred that the relative amount of grafted PEI on the surface of the alumina particles was increased. No significant changes were observed at above 5 wt %, which indicated a saturation point for the grafting.

In Fig. 2, the transients of surface charge and polydispersity index in a suspension of deionized water are investigated for each sample composition. The zeta-potential value of the as-prepared
alumina particles was $-7 \text{mV}$ in pH 6.8. This very low absolute value was due to the negative charge, and indicated no significant direction of the force, which is neutral in view of electrostatics. The PEI treated specimens reversed to a positive charge, and the zeta potential values were 11.2, 24.7, 50.1, 48.4, and 51.0 mV for 1, 3, 5, 7, and 10 wt% of PEI content. The alternation of the surface charge has a profound impact on the behavior of the dispersion of the suspension by applying the force of electrostatic stability. The PDI values of the specimens have identical trends as the zeta-potential transition. The PDI values decrease from 0.78 for the as-prepared alumina particles to 0.08 for 5 wt% of PEI content. PDI is a criterion of the distribution of individual molecular masses in a group of polymers indicative of relation to the width parameter of distribution curve. Between the PDI values from 0 to 1, it is typically considered that a colloidal suspension is monodispersed below 0.1. Because a PDI value of less than 0.1 describes high monodispersity, samples with above a 5 wt% PEI content, which exhibits the highest zeta-potential values, are judged to be the most monodisperse colloidal suspensions. In other words, the driving force of the dispersion behavior is electrostatic repulsion due to the positive surface charge.

Figure 3 shows the particle size distribution parabola of the surface modified alumina particles with various concentrations of PEI. The as-received alumina particles reveal an average size of 178 nm. The particle size for each concentration is gradually reduced when the PEI content is increased from 1 to 5 wt%, until saturation. Each specimen shows an average size of 164 nm for 1 wt%, 122 nm for 3 wt%, 58 nm for 5 wt%, 60 nm for 7 wt%, and 57 nm for 10 wt%. The sharpness of the distribution curves is narrowed in accordance with the size reduction, although all of the specimens have a monomodal pattern. For the as-received alumina particles with the largest average particle size, the colloidal particles are aggregated in the aqueous solvent as a consequence of their high surface energy due to their innately small particle size and nearly neutral surface charge. In contrast, for the PEI treated specimens, agglomeration is controlled because of steric hindrance from the C–H stretching vibration (observed in the FT-IR spectrum) and electrostatic repulsion force of the positive surface charge from the amine group.

Changes in the particle size distributions, zeta-potential, and polydispersity index are not observed for samples with over a 5 wt% PEI content. According to the previous FT-IR measurements, the relative amount of amine groups on the particle increases until reaching 5 wt% PEI additive, which is the optimized amount of PEI content for binding amine groups on the surface of alumina to improve its dispersion capability. In the change curves of the alumina content and apparent porosity with the infiltration time, an increase of the alumina content and decrease of porosity are observed during alumina particle infiltration of the 5 wt% PEI treated sample. The alumina content in the specimen continually increases with infiltration time and reaches a relatively saturated amount, which is 2.54% at 30 min. With an increase in the total content, the apparent porosity naturally decreases to a minimum at the same time. The content of alumina continuously increases with the additional infiltration process and becomes 2.8% at 60 min, unless the increase rate is extremely reduced.

SEM and EDX measurements are conducted for the prepared fused silica and infiltrated specimen for 30 min, as shown in Fig. 5. The fused silica particles have a flack and keen edged shape with agglomeration and are dispersed heterogeneously in the specimen. Thus, there are few pores throughout the specimen, as indicated by the apparent porosity shown in Fig. 4. Compared to the prepared fused silica, alumina infiltration has a critical effect on the porosity because the coagulated alumina particles are homogeneously distributed around the boundary of the silica matrix. The EDX mapping of Si and Al also supports the
densifying behavior of the infiltration. The area of Al detected homogenously is distributed evenly to avoid the Si area.

In conclusion, the infiltration behavior of amine-functionalized alumina colloidal particles is enhanced compared to that of a commercial alumina suspension determined from a previous study, that is, from 150 to 30 min. Although the application time is reduced by more than a half, the same performance is obtained. This enhanced efficiency is expected to be due to the electrostatic attraction force between the negative charge of silica (−42 mV) and the positive surface charge of alumina particles due to amine functionalization. Moreover, the enhanced dispersion of the colloidal suspension is because the alumina particles could move more easily with the movement of the solvent in the infiltration process, regardless of the pore size, compared to agglomerated particles.

As revealed in the X-ray diffraction analysis shown in Fig. 6, phase transformation occurs when sintering fused silica or silica-alumina composites at 1300°C. Each specimen contains zircon (JCPDS 6-266) and cristobalite (JCPDS 39-1425). Because of the low content of alumina, only zircon and cristobalite peaks are found in the specimens infiltrated for 10 and 20 min. After 30 min of infiltration time, mullite peaks (JCPDS 15-0776) are eventually found, which is transformed from fused silica according to following reaction:17

$$3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{Al}_6\text{Si}_2\text{O}_{13})$$

For the specimen infiltrated for over 40 min, alumina diffraction peaks (JCPDS 46-1212) are revealed, which indicate unreacted alumina after sintering at 1300°C due to the excess amount of alumina infiltrated.

To examine the effect of alumina infiltration on the mechanical property, the flexural strength and linear shrinkage of the specimens with respect to the infiltration time are obtained. The densities of non-infiltrated and 30 min infiltrated specimens after sintering were 2.662 and 2.669 g/cm³, respectively. The error range of those specimens were both ±0.003. The differences in density are minimum 0.001 g/cm³, and maximum 0.013 g/cm³. Therefore, the densities of those two specimens were almost same as each other. In the case of the non-infiltrated specimen, the flexural strength and amount of shrinkage are, respectively, 3.2 MPa and 1.91%. On the other hand, the flexural strength of the infiltrated specimens is larger and the amount of shrinkage is smaller than that of the non-infiltrated specimen. As shown in Fig. 7, the flexural strength is gradually enhanced up to 10.2 MPa until 30 min of infiltration time. In addition, the amount of shrinkage is also gradually decreased up to 1.05%. However, above 30 min of infiltrating time, no significant changes are found for the flexural strength and amount of shrinkage with the changing alumina content. Therefore, the improvement of the flexural strength using the infiltration process is limited for times above 30 min.

4. Conclusion

PEI surface modified colloidal alumina was infiltrated in a silica-zircon composite to enhance its mechanical properties as a ceramic core. By functionalization with amine groups via grafting of PEI, the zeta potential of the colloidal alumina was increased to 35 mV, and the dispersity in water clearly increased with changes in the surface properties, that is, from 178 to 58 nm for the average size and 0.78 to 0.08 for the PDI value, which implied monodispersity at a 5 wt% PEI content. Therefore, the adsorption ability of the alumina particles onto the surface of silica via the attraction of opposite electrical charges was highly accelerated, and steric hindrance resulted due to the Câ–H chain. As a result, the infiltration time for the saturated alumina content of 2.5% was reduced up to 30 min, accompanied at the same time by a decrease of the apparent porosity to a minimum value. As the colloidal alumina infiltrated in the pre-sintered specimen, the flexural strength improved up to 10.2 MPa and the amount of shrinkage decreased to 1.05% via mullitization between alumina and silica to prevent the surface crystallization of cristobalite. However, excessive alumina existed above 30 min of infiltration time and did not react with the fused silica; thus, the effect of improvement in the flexural strength was limited to a certain degree.

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