Rapid Communication

Effects of Different Forming Methods on the Properties of Solidified Body by Non-firing Process Through the Mechanochemical Treatment

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Received April 17, 2012

SYNOPSIS

A “non-firing ceramic process” for producing high-strength ceramic solids without calcination is developed. In this process, a ceramic powder, activated by mechanochemical processing, is dispersed in an alkaline solvent to dissolve any metallic ions in the powder and to form precipitates between grains via reprecipitation. The ash powder of the incinerated paper sludge (PS ash, waste generated during paper recycling) is subjected to mechanochemical processing using a planetary ball mill, and non-fired compacts are prepared by wet forming or dry press forming; the effects of different forming methods on the compact properties are investigated. The compacts obtained by the wet forming had a low mechanical strength because the impurities in the PS ash reacted with KOH, resulting in gas emission during solidification and thus in the fracture of already solidified matter through the expansion of gas volume. However, dry press forming yielded good-quality compacts with few defects such as pores and cracks because only the minimum amount of the powders surface necessary for solidification was dissolved and reprecipitated, limiting the excessive dissolution of powder by the KOH solution.

KEY WORDS

mechanochemical treatment, surface activation, paper sludge ash, eco-friendly technique

1 Introduction

Ceramic materials, from traditional porcelain (e.g., tableware, tiles, sanitary ware, insulators) to fine ceramics, ceramics are fundamental and versatile materials that are indispensable to human life today. The synthesis of ceramics requires firing at high temperatures for long periods. In the ceramics manufacturing process, which consists of mixing raw materials, casting, drying, and firing, a large amount of energy is consumed in the firing process.

With the recent changes in market needs, however, synthetic raw materials are being increasingly used instead of natural raw materials. Various organic binders and plasticizers are being added as aids instead of the conventional and natural kaolin, which has good plasticity and firmness, thus increasing the dependence on organic materials. However, the organic matter in a compact must be removed by thermal decomposition during the firing process, but the use of more energy resources and the deterioration of the environment by volatile organic compound (VOC) gas emissions are becoming important social issues. In addition, large amounts of greenhouse gases are emitted during the manufacture of ceramics; the CO₂ emissions from energy consumption during the

manufacture of ceramics in Japan exceed three million tons per year^{1,2)}.

Therefore, “firing at high temperature” and “forming by adding organic matter” are necessary in the manufacturing of ceramics today. There has been no resolution toward the achievement of a low-carbon society, and the development of revolutionary technology is necessary.

More than one million tons of paper sludge (PS, waste generated during recycling of waste paper, water content of about 65 %) is generated each year in Japan. Most PS is incinerated to reduce its volume, using fuels such as used tires. About 200,000 tons of incinerated PS ash powder (PS ash) is generated each year, most of which is disposed of in landfill sites, causing environmental problems. Calcium carbonate and kaolin are added to bleach and wash paper fibers during paper recycling. Therefore, the resulting PS ash contains various metal oxides³⁾, and these resources may be useful³⁻⁶⁾.

We focused on the peculiarities of particles activated by mechanochemical processing. We dispersed activated ceramic powder in an alkaline-containing solvent to dissolve the metallic ions from the powder and form precipitates between the grains through reprecipitation mechanisms and

thus succeeded in developing a “non-firing ceramic process” that gives high-strength ceramic solidified body without calcination^{7–9)}. The PS ash used in this study contains various metal oxides, as explained earlier, and has a large metal content. Therefore, the formation of compacts using the “non-firing ceramic process” is plausible, and this method has numerous potential applications, for example, in producing building materials. In this study, we performed mechanochemical processing of PS ash using a planetary ball mill, prepared non-fired compacts by wet forming or dry press forming, and investigated the effects of different forming methods on compact properties.

2 Experimental details

PS ash⁸⁾ was used as the sample in this study. Mechanochemical processing was performed using a planetary ball mill (P-5, Fritsch Corp.). For the mechanochemical processing, zirconia balls and pots were employed. The revolution rate was fixed at 5 s^{-1} , the milling time was varied between 600, 1800, 2700, and 3600 s, and the ball size was 5 or 10 mm. The obtained activated powder was wet-formed, press-formed. For wet forming, a slurry with 60 wt% solid content was prepared using 3 mol/L KOH solution. This slurry was mixed for 360 s using an electric mixer (AR-250, THINKY Corp., Japan), sealed in a Teflon mold with dimensions of $80 \times 10 \times 80\text{ mm}$, and kept for 86400 s at room temperature to solidify the slurry. The solidified material was removed from the mold and dried for 86400 s at 40°C . For press forming, a slurry with 80 wt% solid content was prepared by mixing the powder and 3 mol/L KOH solution, and the granular samples were sieved (#20) and pressed under a pressure of 80 MPa. The solidified material was retained in the nylon bag for 86400 s at room temperature. The solidified material was removed

from the nylon bag and dried for 86400 s at 40°C . The properties of the compact were assessed through appearance evaluation with a charge coupled device (CCD) microscope, internal structure evaluation by X-ray computed tomography (X-CT) observation, microstructure evaluation by scanning electron microscopy (SEM), and a three-point bending strength test using a precision universal testing machine (AGS, Shimadzu).

3 Results and discussion

The PS ash was processed mechanochemically using a planetary ball mill. The non-fired compacts were formed by wet and dry press forming, and the effects of different forming methods on the compact properties were investigated. Figure 1 shows the appearances and CCD microscope images of samples obtained by wet forming of the mechanochemically processed powder. Both samples in the figure show many dimples on the compact surface and the presence of numerous cracks. Figure 2 shows the

Fig. 1 Appearances and CCD microscope images of samples obtained by wet forming of the mechanochemically processed powder for 3600 s. (a) and (c); ball size of 5 mm, (b) and (d); ball size of 10 mm.

Fig. 2 The microstructure of the fracture surface observed using SEM. (a) the mechanochemically processed powder (ball size 5 mm, milling time 3600 s) before mixing with KOH solution, (b) the mechanochemically processed powder (ball size 5 mm, milling time 3600 s) after mixing with KOH solution, (c) the mechanochemically processed powder (ball size 10 mm, milling time 3600 s) after mixing with KOH solution.

microstructure of the fracture surface observed using SEM. The surface of the mechanochemically processed powder (ball size: 5 mm, milling time: 3600 s) before mixing with the KOH solution (Fig. 2 (a)) was smooth, but the photos of the compact fracture surface after reaction with the KOH solution (Figs. 2 (b), (c)) show edge-shaped precipitates at the powder interfaces, indicating that these precipitates bind the powder together. The amount of precipitate was larger in the powder mechanochemically processed with 10 mm balls. This powder contained grains angular in shape, which is different from the shape observed before mixing with the KOH solution.

Figure 3 shows the results of the bending strength tests of the compacts. The samples using the raw powder material did not solidify, and therefore, the bending strength could not be measured. The bending strength was about 1–2 MPa for the compacts of the mechanochemically processed powder, and no relation was found between the mechanochemical processing conditions and the mechanical strength.

Figure 4 shows X-CT images of samples that were mechanochemically processed for 3600 s using a planetary ball mill with different ball sizes. The many dimples on the surface of the compact in Fig. 1 were also found to exist

Fig. 3 The results of the bending strength tests of the compacts obtained by wet forming.

Fig. 4 X-CT images of solidified body obtained by wet forming. (a) ball size of 5 mm, (b) ball size of 10 mm.

as pores in the compact. There were many cracks in the compact extending from the pores. The PS ash used in this study consists of a wide variety of matter: calcium carbonate and kaolin used for bleaching and washing in the recycling process, steel wires in the used tires used as fuel when reducing the volume through incineration, un-decomposed and carbonized cellulose (the main component of paper fibers), and unknown impurities. We speculate that some gas was formed during solidification after mixing with the KOH solution, and the volume expansion of this gas fractured the already solidified matter, although we could not identify the gas. As a result, although many edge-shaped precipitates formed at the powder interfaces, binding the powder together, the mechanical strength of the compact was low and there was no relation between the mechanochemical processing conditions and the mechanical strength.

Figure 5 shows external images and CCD microscopy photos of the surface structures of samples obtained by press forming of the mechanochemically processed powder. The many dimples and cracks seen on the surface of the compact in Fig. 1 were not observed in either of these samples, and the surfaces were smooth. Figure 6 shows the fracture surface microstructure observed by SEM for the samples prepared by press forming of the mechanochemically processed powder. The photo of the compact fracture surface of the powder mechanochemically processed using 5 mm balls (Fig. 6 (a)) does not show edge-shaped precipitates at the boundaries of the powder, as were seen in the wet-formed compacts. On the other hand, in the sample of the mechanochemically processed powder using 10 mm balls, some edge-shaped precipitates at the

Fig. 5 Appearances and CCD microscope images of samples obtained by dry pressing of the mechanochemically processed powder for 3600 s. (a) and (c); ball size of 5 mm, (b) and (d); ball size of 10 mm.

Fig. 6 The SEM photographs of microstructure of the fracture surface obtained by dry pressing. (a) ball size 5 mm, (b) ball size 10 mm.

Fig. 7 The results of the bending strength tests of the compacts obtained by dry pressing.

boundaries appeared (although the amounts were smaller than in the wet-forming samples), and these precipitates bound the powder. Figure 7 shows X-CT photos of samples prepared by press forming of the mechanochemically processed powder. There were no major defects such as pores and cracks arising from gas formation during solidification, as were observed in the wet-formed samples. The reduction in the amount of the added KOH solution and the press forming of granular samples led to an optimum ratio of the KOH solution to powder, which dissolved the minimum amount of the powder surface necessary for reprecipitation and solidification, suppressing excessive dissolution of the powder by the KOH solution that would result in the emission of gases and the formation of defects such as pores and cracks.

Figure 8 shows the results of the bending strength tests of samples prepared by press forming of the mechanochemically processed powder. The press-formed samples had higher mechanical strengths than the wet-formed samples shown in Fig. 3; the powder that was not mechanochemically processed solidified, and its bending strength was about 3.8 MPa. The powder that was mechanochemically processed with 10-mm balls had a bending strength about 1.5 times that of the press-formed samples obtained using the raw powder material. The strength did not change much with

Fig. 8 X-CT images of solidified body obtained by dry pressing. (a) ball size of 5 mm, (b) ball size of 10 mm.

increasing processing time. On the other hand, the samples using powder that was mechanochemically processed with 5 mm balls had almost the same bending strengths as the press-formed samples using the raw powder material, so no effect of the mechanochemical processing on bending strength was evident. These results show that a difference in ball size affects the mechanochemical effects and the compact properties. There was no change in compact strength with increasing mechanochemical processing time with the PS ash used in this study. Mechanochemical processing would be easier and the effects would appear with shorter processing times with PS ash, because it is intrinsically softer than typical ceramics (e.g., alumina, zirconia).

In summary, the mechanical strength was found to decrease when the mechanochemically processed PS ash was wet-formed, because a gas is emitted during the solidification process and an increase in the gas volume causes the already solidified matter to fracture. In contrast, press forming of the mechanochemically processed PS ash resulted in the synthesis of good compacts with few defects (pores and cracks) that accompany gas formation, because only the minimum amount of the powder surface necessary for solidification was dissolved and reprecipitated, limiting the excessive dissolution of powder by the KOH solution.

4 Conclusion

We processed PS ash mechanochemically using a planetary ball mill, prepared non-fired compacts by wet forming or dry press forming, and investigated the effects of the different forming methods on the compact properties. The samples obtained by wet forming had low mechanical strengths because impurities in the PS ash reacted with

KOH, resulting in the emission of gas during solidification and the fracture of already solidified ceramics because of the volume expansion of this gas. Good samples were obtained through dry forming because only the minimum amount of the powder surface necessary for solidification was dissolved and reprecipitated, limiting the excessive dissolution of powder by the KOH solution. Therefore, the resulting compacts had few defects such as pores and cracks. Changes in the mechanochemical effect were seen when the ball size was changed, which also affected the compact properties.

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