Microwave-Reactive Organic Binder for Ceramics Forming

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Abstract: Because the pyrolysis of organic substances can result in the emission of carbon dioxide or other hydrocarbon gases, a reduction in the use of organic binders is one aim of current ceramics industry. A novel ceramic-forming process was developed that requires considerably less organic binder than conventional techniques. The process involves immobilizing reactive molecules on the surfaces of the particles, which on subsequent irradiation with microwaves, form bridges that bind the entire particle assembly together. The chemical forces involved produce strong bonds, resulting in a significant reduction in the amount of organic binder that is required to maintain the shape of the ceramic green body.

Keywords: Green body, Organic binder, Microwave, Eco-friendly process

1. INTRODUCTION

In ceramic processing, organic substances are often used as binders, dispersants, plasticizers, or lubricating agents [1]. However, these must be removed before the sintering process by converting them into carbon dioxide and hydrocarbon gases, which are emitted into the environment. As a result of serious global environmental problems, all manufacturing industries are being forced to pay more attention to reduce the emission of pollutants. The current trend in the ceramic industry is to protect environment by reducing the amounts of organic additives that are used.

Binders are traditionally employed in the shaping of ceramic materials because of their non-plastic nature. A conventional organic polymer binder functions by absorption onto the surfaces of ceramic particles that otherwise have insufficient mutual binding forces; however, a poor affinity between the binder molecules and the ceramic particle surfaces will result in phase separation and inhomogeneous partial segregation, which impair the function of the binder. The phase separation results in non-uniform microstructures in green bodies and may result in defects such as cracks and voids in sintered bodies [2]. Weak bonding by the binder and subsequent phase separation necessitate the use of disproportionately large amounts of organic binder.

In the present study, we prepared ceramic green bodies using a reactive organic binder which anchor covalently on the particle surfaces. Stronger bonding of the organic binder prevents phase separation between the ceramic particles and binder. The resultant green body contains only minimal amount of organic binder. In the forming process, ceramic particles should be able to merge mutually in an arbitrary stage. We investigated the utilization of microwave irradiations as a trigger for mutual binding reactions.

2. MATERIALS AND METHODS

In the present study, a macromolecule containing carbodiimide groups (-N=N-) and water-attracting (hydrophilic) segments in its structure was employed as a linking agent to form the particle assembly. Hereafter the macromolecule will be referred as water-dispersible polycarbodiimide (WDC). The carbodiimide group can react with a variety of chemicals [3-5]. When green bodies containing WDC within their structure are irradiated with microwaves, water molecules near the hydrophilic segments are dielectrically heated in a time-efficient manner. Subsequently, the increase in the internal temperature of the green bodies induces a reaction of the carbodiimide groups. By this method, we prepared green bodies composed of mutually connected ceramic particles by using microwaves as the reaction trigger.

Spherical silica particles were used as the ceramic phase. The number-average diameter of the particles was 270 nm, as observed by transmission electron microscopy. The silica particles were treated with aqueous solution of (3-Aminopropyl)triethoxysilane [3-APS; H₃N(CH₂)₃Si(OCH₂CH₃)₃] to obtain silica particles whose surfaces were covered with amino groups (–NH₂) [6-8].

3-APS-coated silica was dispersed in ultra-pure water by using intense agitation. WDC (molecular weight: 2000) was added to the suspension to link the 3-APS-coated silica particles. The slurry was formed by slip casting into tablets of 10 mm diameter and 2 mm height, and into rectangular 10 × 10 × 4 mm solids. On irradiation with the microwaves, the WDC forms covalent bonds with the amino-functionalized silica, binding the particles together: the carbodiimide group reacts with the amino group to form a guanidine structure when it is heated to ~80 °C (Fig. 1) [9]. Microwave irradiation was carried out in a tunable magnetron multimode microwave furnace. The green bodies were placed in a thermally insulated box and irradiated with 200 Wh of microwaves at 2.45 GHz in the presence of microwave-absorbing dummy loads.

3. RESULTS AND DISCUSSION

In IR spectrum of WDC, a diagnostic band from carbodiimide stretching is found at 2120 cm⁻¹. IR diffuse reflectance spectra of the microwave-irradiated green bodies in the carbodiimide stretching region are
Binding mechanism of a polycarbodiimide reactive segment with amino group upon microwave irradiation:

![Binding mechanism diagram]

Figure 1. Binding mechanism of a polycarbodiimide reactive segment with amino group upon microwave irradiation.

When carbodiimide groups are heated to ~80 °C, they initiate bonding to neighboring amino groups on the silica surface, and this reactivity can be used to form covalent linkages between the particles. Decreases in the strength of the carbodiimide absorption bands can be used to monitor the progress of the reaction: the intensity of the absorption band decreased with increasing time of microwave irradiation. The change in the intensity of the absorption band indicated the formation of linkages between the silica particles.

![Spectral changes diagram]

Figure 2. Spectral changes in the carbodiimide absorption band during microwave irradiation. The elapsed time are 0, 5, 10 and 20 min, from top to bottom.

We prepared two kinds of green bodies, one with and one without covalent linkages. The former was a green body containing WDC treated by microwave irradiation for 20 min, and the latter was a green body prepared in the same way, but using poly(ethylene glycol) (PEG) instead of WDC. PEG is composed solely of the hydrophilic segments and contains no carbodiimide segments. Because there is no chemical bonding between the silica particles, the PEG-containing green body can be used as a control specimen. The two kinds of specimen were soaked in water and kept for a long period. Remaining air in the green bodies was expelled by keeping the whole assembly under a reduced-pressure atmosphere. Green bodies with no attractive force other than capillary condensation acting between the constituent particles should not be able to maintain their shapes. Whereas the control specimen collapsed immediately on soaking in water, the green bodies with covalent linkages maintained their shape in water (Fig. 3).

![Photographs of green bodies]

Figure 3. Photographs of the green bodies prepared by using PEG and WDC. The green bodies were soaked in water to evaluate the advantageous effect of the interparticle bonds.

The mechanical properties of the green bodies were evaluated by using a universal testing machine. Because the green bodies were not subjected to any firing process, the usual mechanical evaluation methods for ceramic sintered bodies were not applicable. Hence, in our study, we employed a simplified breaking test. The total weight on the load cell was recorded when the push-pin broke the rectangular green bodies. We tested 18 specimens of green bodies containing WDC and a similar number of control specimens and recorded the weight values when the green bodies were broken. The results are summarized in Fig. 4. The mechanical strength of
the control specimen was, naturally, poor. Disintegration began at a load of about 500 g. Disintegration of the green bodies with the chemical bonds occurred at loads of more than 1000 g, and the mechanical properties of these green bodies were significantly better than those of the control specimens.

Figure 5 shows typical burnout profiles of the WDC-containing green body, measured by thermogravimetry (TG) analysis. The majority of the organic substances in the green body were removed between 200 and 600 °C. Therefore, the shapes of the green bodies were maintained in the presence of only 0.6 mass% of organic substances, which is much less than required for conventional polymer-based molding systems. With such a small amount of binder, green bodies are usually too fragile to handle. Therefore, the present method, through linking of the particles induced by microwave irradiation, results in a marked reduction in the amount of organic binder that is required compared with that used in conventional methods.

![Figure 5. TG curve of the WDC-containing green body. The region relating to the burning out of organic substances is magnified.](image)

After the water-soaking test, the green bodies taken out of the water could be cut with a razor blade. This unique ability could be ascribed to a concerted effect of the mutual covalent linkages and capillary condensation forces due to water adsorbed within the green body between particles. The organic constituents forming interparticle bridges should be accompanied by considerable numbers of water molecules. The covalent bridge, assisted by the capillary condensation force, withstands the internal stress caused by the intrusion of the razor blade and prevents the disintegration of the whole green body. Consequently, the green body can be cut with ease. When the cut surfaces were re-exposed to water, there was no observed disintegration in the sample, either by removal of particles from the surfaces or by rounding off the edges.

4. SUMMARY
A novel ceramic-forming process was proposed. Microwave-reactive organic molecule was used to form bridges to bind the entire particle assembly. The resultant assembly can be considered as a ceramic green body. This unique methodology results in a significant reduction in the quantity of organic binder that is required to maintain shape, while providing a stronger binding as a result of the chemical forces that are involved. The green body obtained in this study displayed improved mechanical properties in the presence of only minimal amount of organic substances. The present method should surely contribute to a reduction of organic binders required for green body preparation when compared to the currently utilized conventional methods.

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REFERENCES