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Binder burnout and evolution of the mechanical strength of dry-pressed ceramics containing poly(vinyl alcohol)

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Abstract

This paper describes the effect of binder removal on the mechanical strength of alumina green samples. These products were prepared by uniaxial pressing of powders spray-dried with poly(vinyl alcohol) used as a binder. Change in mechanical strength of these compacts was studied during thermal debinding. The behaviour was investigated by means of thermogravimetry, DSC and FTIR spectroscopy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Binders; Green strength; Microstructure-prefiring; Pressing

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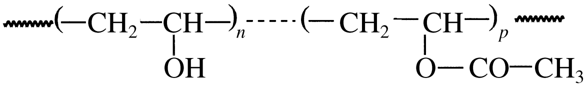
1. Introduction

Binders are often added in ceramic processing that involves spray-drying of slurries followed by dry-pressing. The addition of these organic polymers is necessary to confer adequate cohesive strength to the sprayed granules[1] and, hence, free flowing properties.[2] Moreover, organic binders improve the strength of the green compacts,[2] although they can affect the relative density.[3–6] The selection of organic additives must then be appropriate to enhance the mechanical strength of green bodies without causing microstructural defects in the ceramic pieces during the debinding step.[7–9]

Poly(vinyl alcohol) (PVA) is largely used as a binder in dry pressed ceramics.[10] We have recently studied the effect of PVA on the mechanical properties and on the density of dry-pressed alumina green products.[11] PVA is prepared by alcaline or acid hydrolysis of pol(vinyl acetate), that usually leaves a small fraction of the acetate side groups (~10 mol%). These residual groups stabilise the polymer (PVA)[12] by preventing the depolymerisation reaction. The PVA structure is given below:



$$\sim\!\sim(-CH_2-\underset{OH}{CH}-)_n\cdots\cdots(-CH_2-\underset{O-CO-CH_3}{CH}-)_p\sim\!\sim$$

Despite the recent development of other binder removal techniques such as microwave treatment[13] and solvent extraction,[14] thermal removal remains the predominant method used in the ceramic industry.[15,16] Burnout usually takes place in oxidising atmosphere at moderately elevated temperatures and, in general, becomes complete by 600 to 700°C for pure polymers and sometimes at higher temperature in presence of ceramic powders.[17] Thermal decomposition of PVA (containing 20 mol% residual acetyl groups) has been studied by Dunn et al.[12] Two reactions can occur, (i) elimination of water and acetic acid which accounts for at least 80% of the weight loss, and (ii) depolymerisation giving acetaldehyde, crotonaldehyde and higher unsaturated aldehydes, this reaction accounting for less than 20% of the total weight loss. Due to many reasons, the decomposition of binder in a green ceramic body is more complex than the decomposition of a pure thin polymer film.[18] Thermal debinding can play a critical role in the properties and in the reliability of the final parts. The aim of this work is to investigate the relation between the strength of alumina pressed samples during

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thermal debinding and the thermal degradation of the PVA which is used as a binder.

2. Experimental procedure

The ceramic powder used in this study was alumina (P152SB Pechiney, France). The specific surface area and the mean particle size were 3 m^2 g^{-1} and 1.3 μm, respectively. A dispersant (DarvanC, Vanderbilt, UK, $M_w = 10{,}000$) known to contain carboxylate groups like PMA-NH_4^+ was used to prepare the spray-drying slurry. The binder added to this slurry was poly(vinyl alcohol) (PVA 4-88, $M_w = 31{,}000$, degree of hydrolysis = 88 mol.%, Hoescht, D). The aqueous suspension containing 60 wt.% P152SB alumina, 0.16 wt.% Darvan C, and 3 wt.% PVA 4-88 on a dry weight basis of alumina, was spray-dried in a pilot plant. The mean size of spray-dried granules was about 200 μm. The flow rate and the temperature of the inlet air were stabilized in the spray-dryer to obtain a residual moisture content of 0.8 wt.% with respect to alumina. This content of residual moisture was verified by thermogravimetric analysis (TGA) for the spray-dried powder.

The glass transition temperature (T_g) of dry PVA is equal to +79°C.[18] Considering that water is only absorbed in the organic phase, moisture of 0.8 wt.% corresponds to a relative content of water in the binder greater than 25 wt.%. According to the results reported by several authors,[10] the T_g of such a water plasticized PVA should be somewhat below room temperature.

The as-received and spray-dried alumina powders were pressed uniaxially at room temperature under 100 and 70 MPa, respectively, to produce disk-shaped samples (30 mm diameter, about 6 mm thickness). Under these pressures, all the samples have a relative density of about 57%. The pressure was released immediately once the desired value was reached, and the sample was ejected. The strength of the green samples was measured by the diametral compression test.[19] These measurements were performed with a universal testing machine at a loading rate of 0.5 mm mn^{-1}. The strength was calculated according to the following expression:

$$\sigma_r = 2\ F_{max}/\pi De \tag{1}$$

where F_{max} is the load applied at fracture while D and e are the diameter and the thickness of the sample, respectively. These mechanical measurements were done immediately after forming because an earlier work showed that strength varies with time after ejection.[2] The values of the strength reported here correspond to the average obtained after three tests.

The evolution of the strength of green samples with temperature were conducted on samples pressed until a relative density of about 57% and heated in air up to various temperatures for 10 min at a constant rate (10°C mn^{-1}). The samples were then cooled rapidly down to room temperature and used to measure the strength by the diametral compression method. This analysis was conducted on samples, prepared from the as-received alumina (P152SB) and from the spray-dried alumina powder containing 3 wt.% PVA 4-88.

Thermal decomposition of the organic phase in the spray-dried alumina powder and in the pressed sample was studied by several methods such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and infrared spectroscopy (FTIR).

Standard TGA and DSC analysis were performed in air (flow rate 5 l h^{-1}) at a heating rate of 10°C mn^{-1} on the spray-dried alumina powder containing 3 wt.% PVA 4-88, and on alumina compacts prepared from the same spray-dried powder, with a relative density about 57%.

In order to study the chemical changes occurring during PVA pyrolysis, the spray-dried powder was heated and analysed by FTIR at various temperatures, 100, 200, 300, 400, 500 or 800°C.

3. Results and discussion

3.1. Thermolysis

Data of thermogravimetric analysis carried out on the spray-dried powder and on a sample pressed at 70 MPa with a relative density of about 57%, are similar (Fig. 1). The forming process induces negligible effects on the binder burnout. In opposition to other binders such as polyethylene glycol which presents a rapid thermal degradation,[20] the decomposition of PVA is gradual and continues over a large range of temperatures. Then, gas resulting from the polymer degradation is able to release more freely within the porosity of the green parts through which it can move to the surrounding atmosphere.

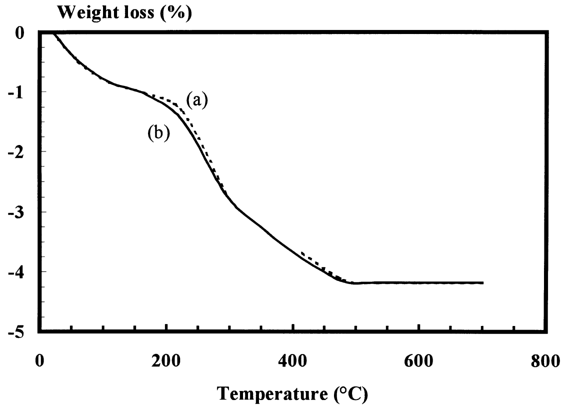

Fig. 1. TGA of (a) the spray-dried alumina powder containing 3 wt.% PVA and (b) of a sample prepared from the same powder by uniaxial pressing at 70 MPa with a relative density about 57%.

The total weight loss amounts to 4.2 wt.%. This value includes elimination of absorbed water (~1 wt.%), dispersant (~0.16 wt.%) and binder (~3 wt.%).

According to the TGA and DSC plots obtained on the spray-dried powder (Figs. 1 and 2), the degradation of PVA can be divided into three stages versus temperature. The initial endothermic reaction up to 200°C corresponds probably to the outgassing of water trapped as a moisture within the binder. There is no significant change in the IR spectra obtained with the spray-dried powder treated at 100 and 200°C (Fig. 3).

After heating to almost 400°C, DSC plot shows a second important endothermic peak and TGA plot shows a weight loss of almost 2.5 wt.%. If we neglect the amount of dispersant compared to that of the binder, this weight loss of the polymer at this burnout stage corresponds to almost 83 wt.% of the amount introduced. Then the greater proportion of the PVA decomposition occurs during this stage.

In order to understand the decomposition mechanism of PVA in the ceramic, the transmission bands, observed in the FTIR spectra (Fig. 3) of the alumina spray-dried powder around 2925 cm^{-1}, 2853 cm^{-1}, 1725 cm^{-1}, and 1630 cm^{-1} and attributed to C–H (in –CHOH–), C–H (in –CH$_2$–), C=O and C=C valence vibrations respectively, were studied after treatments at different temperatures. Figs. 4 and 5 show the evolution with temperature of the ratio between the areas of the first and the second C–H band (Fig. 4), and of the areas of the C=O and C=C bands (Fig. 5). It is clear that the loss of C–H and C=O bands occurs approximately in the range of temperatures between 200 and 400°C, whereas the area of the C=C band increases in the same range of temperature. Then, the weight loss in this second stage can be attributed to the elimination of water and acetic acid from PVA chains as illustrated in Fig. 6.

Above 400°C, the exothermic behavior observed in the DSC plot corresponds to a reaction of depolymerisation and oxidation of the vinyl chains (Fig. 6). In fact, the C=C band area decreases rapidly up to 500°C then more slowly up to 800°C (Fig. 5).

According to these last results, the decomposition of the polymer continues at temperatures higher than 500°C despite the fact that the TGA data indicate no

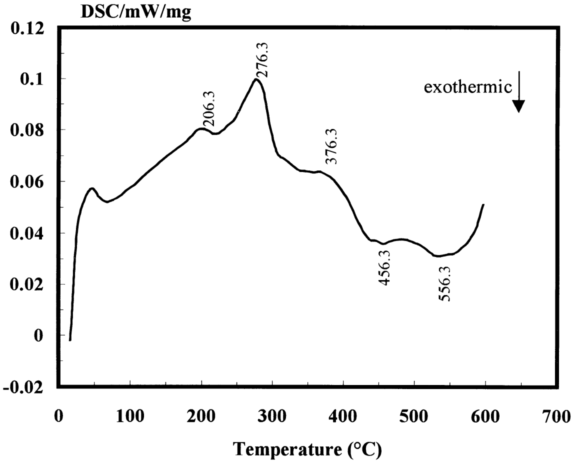

Fig. 2. DSC of the alumina spray-dried powder.

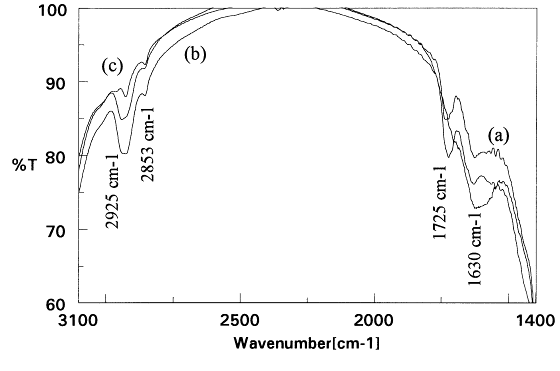

Fig. 3. FTIR spectra of the spray-dried powder after treatment at (a) 100°C, (b) 200°C and (c) 300°C.

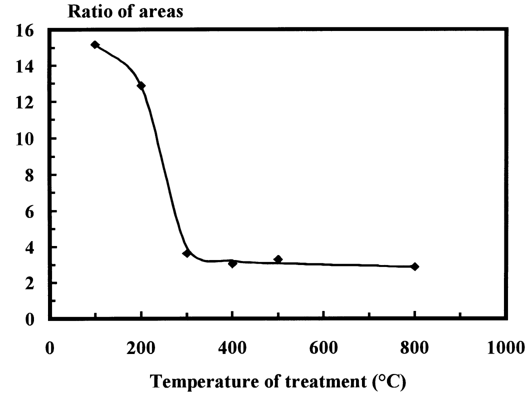

Fig. 4. Evolution of the area ratio of the C–H bands in FTIR spectra versus temperature of treatment.

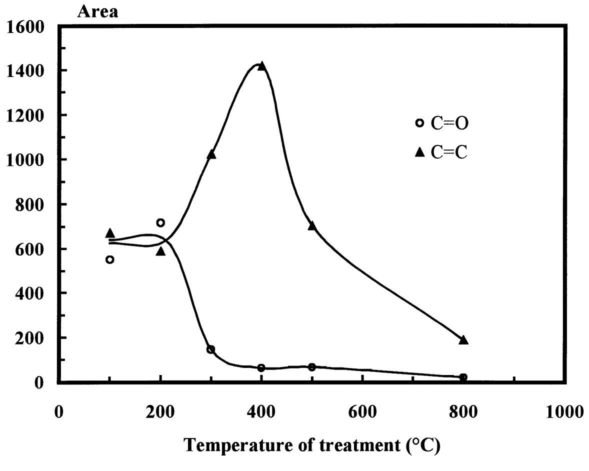

Fig. 5. Evolution of C=O and C=C area bands in FTIR spectra versus temperature of treatment.

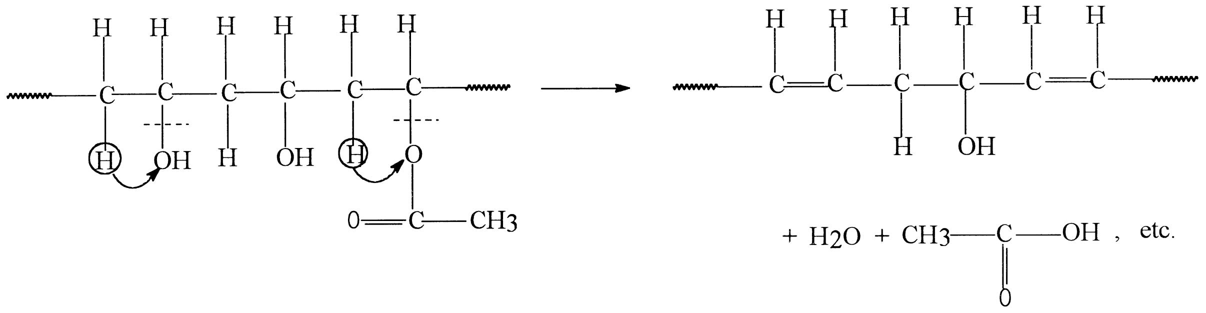

Fig. 6. Schematic of the elimination of water and acetic acid from PVA during the second phase of TGA.

weight loss above 500°C. This suggests that a low carbonaceous residue remains in the alumina sample after treatment at high temperature ($T > 500$°C), in agreement with the results of Ferrato.[21]

3.2. Mechanical strength

Significant variations were observed for the mechanical strength according to the temperature of thermal treatment of alumina pressed samples, prepared from the as received and from the spray-dried alumina powders (Fig. 7).

There is no doubt that the binder enhances the strength of green compacts at room temperature. In an earlier work,[22] it was concluded that the organic binders, especially those which are water soluble, tend to migrate with the liquid flow which occurs during the spray-drying process of the ceramic suspension and then segregate to the surface of the granule to form a polymer-rich layer. The thickness of this layer, which contains about 50% of the binder introduced, was estimated to a few percents of the granule radius. Then, the strength of pressed green products results from a compromise between adhesive properties of the polymeric shell covering the granules and the strength of the granule itself. For instance, when the T_g of the binder is lower than the forming temperature, the interdiffusion between polymeric layers leads to strong bonds between granules. Green strength is then controlled by polymer–polymer and polymer–ceramic interactions. Any changes in the polymer properties lead to a change in the mechanical strength of green products.

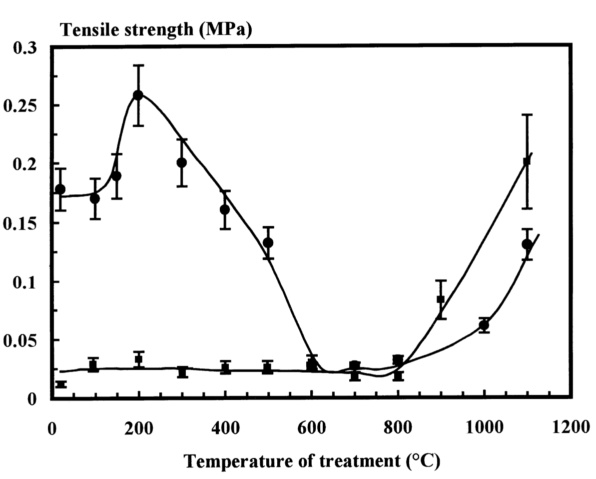

Fig. 7. Evolution of the strength of compacts with a relative density about 57%, prepared from (■) the as-received and (●) from the spray-dried alumina powders, versus temperature of treatment.

The strength of samples obtained from the original alumina remains low and constant (~0.025 MPa) until 800°C. Beyond this temperature the strength starts to increase. The absence of significant cohesive forces between alumina particles explains the low strength observed for pressed samples at low temperature. The strength increase taking place beyond 800°C can be attributed to initial sintering of the ceramic.

In the same range of temperature, the strength of green products prepared from spray-dried alumina powder is more sensitive to the thermal treatment. The evolution can be divided into four stages. In the first phase (20°C $\leqslant T \leqslant$ 200°C) strength increases with temperature from 0.175 to 0.26 MPa. Such a variation coincides with the first weight loss in TGA plot (Fig. 1) which was attributed to the elimination of water absorbed in the sample. It is well known that water acts as a plasticizer for PVA.[10] Plasticization enhances the interdiffusion between polymeric layers but weakens the mechanical properties of the polymer. The observed increase in strength upon heating is then due to the removal of water, resulting in the elimination of this plasticization effect. In the second phase (200°C $\leqslant T \leqslant$ 600°C), strength decreases in the same way as the weight loss in TGA plot (Fig. 1). During this phase, the weight loss was attributed to the thermal decomposition of PVA. The strength decreases slowly down to almost 0.12 MPa at 500°C, which probably corresponds to the elimination of water and acetic acid from the polymer, then more drastically between 500 and 600°C, which corresponds to oxidation of vinyl chains. At a temperature of 600°C, the strength reaches a value close to that of samples prepared from the as-received alumina (i.e. 0.025 MPa). The decomposition of the PVA binder

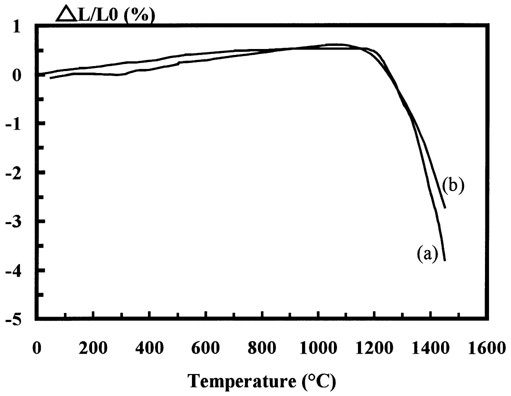

Fig. 8. Dilatometric analysis of a compact pressed until a relative density of about 57%, from (a) the as-received and (b) from the spray-dried alumina powder.

leads to a gradual destruction of the polymeric bridges between alumina particles and/or between granules responsible of the mechanical strength of the compact. In the third phase (600°C $\leqslant T \leqslant$ 800°C), the mechanical strength of green products remains constant at a low value (i.e. 0.025 MPa). Under these conditions, pressed samples are only made of alumina particles free of organic binder. In the final phase ($T >$ 800°C), strength begins to increase in the same way as that of the samples prepared from the as-received alumina but more slowly. According to the thermal dilatometric analysis of compacts prepared from the as-received alumina powder and from spray-dried alumina powder containing 3 wt.% PVA, the densification of both ceramic samples starts at a temperature close to 1100°C which corresponds to the initial shrinkage (Fig. 8). Then, the observed increase of the strength in the final stage (above 800°C) can be explained by the formation of grain boundaries at a temperature below 1100°C, without significant change in the relative density of the compact. The presence of carbonaceous residues in the samples prepared from the spray-dried powder and the difference in the microstructure can be the origin of the sintering delay compared to that of samples prepared from the as-received alumina powder (Figs. 7 and 8).

4. Conclusion

The mechanical strength of green products, pressed from alumina spray-dried powders containing 3 wt.% PVA as a binder, was studied after heat treatments at various temperatures. The strength was observed to vary with temperature. From room temperature to 200°C, the strength increase was attributed to the elimination of absorbed water which plays the role of plasticizer for the PVA binder. In a second stage, at temperatures between 200 and 600°C, the strength decreases in the same way as the polymer weight loss. This behavior was explained by the gradual thermal decomposition of PVA, first the elimination of water and acetic acid, then the depolymerisation and the oxidation of the vinyl chains. DSC and FTIR analysis show that the polymer is not totally eliminated during this stage, and that a carbonaceous residue remains in the sample even after treatment at high temperature. At 600°C, the value of the strength is quite low and comparable to that of samples prepared from the as-received powder. Beyond 800°C, the strength increases again due to the initial stage of sintering which corresponds to the formation of grain boundaries.

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