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A new polyurethane binder providing high green strength of dry-pressed alumina

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Abstract

The effect of a new polyurethane binder on green strength of dry-pressed alumina bodies was studied. The alumina compacts showed exceptionally high green strength. Depending on binder concentration (1–5 wt.%) the tensile and flexural strength were 1.6-7.0 MPa and 2.0–12.7 MPa, respectively. The high green strength was controlled by polymer–ceramics interactions, as was revealed by IR study. The glass transition temperature of polymer influenced the binder behaviour in ceramic processing. To achieve high green density some residual moisture was needed but then samples had to be dried to obtain high green strength. The binder burnout was characterized by TGA and DTA study in air and in nitrogen. The polyurethane binder had a gradual burnout with a low char residue in both types of atmosphere. The thermal decomposition in air was caused by oxidation reactions, while in nitrogen, the polyurethane binder underwent depolymerization process.

Keywords: A. Pressing; D. Alumina; Organic binder; Green strength

1. Introduction

An organic binder is the most important additive in the dry pressing process of advanced ceramic powders. It must fulfil several requirements such as mixability with ceramic powder, adequate granule flow time, adequate glass temperature, high green density, sufficient green strength, low burnout residue, etc. The details are reported in many publications [1–7].

When the pressed part is to be green machined, the most important problem is to determine the binder system providing high mechanical green strength and high green density. The green density is a measure of agglomerates packing and it determines the final density after sintering. The green strength of ceramic part must be sufficient to withstand the conventional machining processes such as grinding, cutting, milling, drilling and lathing. In the case of milling, drilling and lathing, a high green strength is required [8]. Polyvinyl alcohol, probably the most common binder in ceramic industry does not ensure the sufficient high green strength. The green machining using this binder is limited to grinding or cutting. Therefore the major issue in green machining is the selection of a binder system providing sufficient green strength.

In 1995, a polyacrylic binder (Duramax™ B-1031, Rohm & Hass) was developed [8]. This binder provided sufficient green strength to allow shaping of unfired ceramic parts from alumina and silicon carbide by drilling, lathing and grinding. The tensile strength of alumina green compacts with addition of 5 wt.% of polyacrylic binder was 6.5 MPa, much higher in comparison with the green strength of alumina compacts pressed with polyvinyl alcohol, which did not exceed 1 MPa.

In polymer literature [9] there is an information on polyacrylic emulsions based on methylacrylate, methylmethacrylate, 2-ethylhexylacrylate and styrene. These emulsions were used as binders providing high green strength of parts pressed from lanthanum chromite and strontium chromite. The emulsions were ready to use dispersions having 0.05–0.5 μm particles in water. Because the polymers were dispersed and not dissolved, the viscosity was much lower than that of a solution of

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polymer of equivalent molecular weight and concentration. Moreover water is the most environmentally friendly raw material for wetting of ceramic powders.

Next to the water dispersed polyacrylic emulsions, a big hope is also connected with polyurethane water dispersed emulsions. By appropriate selection of substrates it is possible to obtain stable polyurethane emulsions in water [10,11]. Polyurethane emulsions are often obtained without low-molecular emulsifiers and therefore the burnout residue is low. Polyurethane chains could adsorb easily on the surface of ceramic powders due to the presence of hydrophobic groups, those could be coordination centres, creating strong interparticles interactions. Moreover, hydrogen bonding could create bridges between polyurethane chains and ceramic particles causing the green strength of the ceramic part to be high. Keeping this in view we sought a commercial polyurethane dispersion that could be used as a binder providing high green strength and high green density of dry pressed ceramic parts. We preferred to use commercial rather than laboratory prepared dispersion believing the latter have reproducible properties. A polyurethane dispersion based on polycarbonatediol (on the base of cyclohexanedi–methanediol, dimethylolpropane derivative and cycloaliphaticdiisocyanates) was chosen from Zeneca-Resins products [12].

The aim of our study is to determine the effect of polyurethane binder on the green strength and green density of dry-pressed alumina bodies, and also to explain the high green strength by IR study. The thermal decomposition of the polyurethane binder has also been evaluated and discussed.

2. Experimental procedure

2.1. Samples preparation

The alumina powder CT 3000 SG with an average particle size of 0.7 μm was donated by Alcoa Chemie (Ludwigshafen, Germany). The aqueous polyurethane dispersion with 35 wt.% of solid particles was donated by Zeneca Resins (Waalwijk, The Netherlands). Aqueous suspensions containing alumina and polyurethane binder were spray-dried in a laboratory equipment. The quantity of polyurethane binder added varied from 1 to 5 wt.% at 1% step (recounted on solid amount of polyurethane in dispersion) on a dry weight basic of alumina. The mean size of spray-dried granules was about 200 μm. Depending on the binder concentration, the moisture content in granules varied between 2.7 and 2.9%. All samples were formed by uniaxially pressing at 150 MPa using a hand-operated hydraulic press. In order to determine the effect of residual moisture content in pressed samples on their mechanical strength two series of samples were tested:

i. Samples were tested immediately after pressing (moisture content 2.7–2.9%).
ii. Before mechanical test samples were dried at 80 °C for 4 h and the residual moisture content were determined as 0.2–0.4%.

2.2. Characterization methods

The mechanical strength of pressed green samples was evaluated by measuring tensile strength and flexural strength. The tensile strength was determined by a diametral compression method so-called 'Brazilian test' [13]. The disk-shaped samples for diametral compression had a diameter of 29 mm and thickness of about 9 mm. The flexural strength was determined from three-point bending. The pressed bars 75×7×9 mm were used and the span was 50 mm. The crosshead speed was 0.5 mm/min for all samples. A universal testing machine FP100, TIRA Rauenstein was used.

The tensile strength of samples δ_t was calculated using the following expression:

$$\delta_t = 2F_{max}/\pi Dh \quad (1)$$

where F_{max} is the load applied at fracture, D and h are the diameter and thickness of the sample, respectively.

The flexural strength δ_f was calculated from:

$$\delta_f = 3F_{max}l/2h^2b \quad (2)$$

where l is the span, h and b are the thickness and width of the bar, respectively.

The reported tensile and bending strengths were the averages of at least five determinations.

The green density was calculated from the weight and dimensions of a minimum of five pellets. The dimensions were measured with a digital calliper accurate to ±0.01 mm. The pellets weight was accurate to ±0.0001 g and was corrected for organic and moisture content of the sample.

The glass transition temperature T_g of polymer was measured by differential scanning calorimetry (DSC, type-822^E, Mettler Toledo). Films were prepared by casting the aqueous dispersions of polyurethane on a Teflon™ surface and allowing them to dry at room temperature and than at 60 °C in vacuum. Prior to the measurements the samples were kept in a desiccator to avoid any moisture. DSC experiments were conducted in the range −80 to +150 °C at 10 °C/min.

The polymer to ceramics interactions were studied by IR spectroscopy.

The thermal decomposition of polyurethane binder was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA and DTA measurements were conducted in air and in nitrogen at

heating rate of 10°C/min. The preparation of polyurethane sample was analogous to that for DSC analysis.

The burnout residues were obtained by thermolysis of bulk samples in air and in nitrogen in a horizontal tube furnace.

3. Results and discussion

3.1. Green density and green strength

The glass transition temperature T_g of a polymer binder is one of the most important parameters controlling binder performance during dry pressing [14]. The T_g affects the green density and the green strength of dry pressed ceramic parts. The T_g of the polyurethane binder was determined by DSC method as +28 °C. Because the T_g of polyurethane binder was several degrees higher than the pressing temperature (20 °C) it required plasticization for obtaining a good compaction. We decided to take advantage of the placticizing effect of water by using the granules with 2.7–2.9% of moisture content. Depending on binder concentration (1–5 wt.%), the green density varied between 59 and 57% of the theoretical density of corundum (3.98 g cm^{-1}) as is shown in Fig. 1. The green density decreased with increasing of a polyurethane binder concentration. The volume occupied by the binder phase causes separations of ceramic particles, leading to the observed density decrease with added binder. For comparison, the powder was dried to about 0.8% of residual moisture and the green density of pressed samples were between 48 and 51% t.d. (Fig. 1). So to achieve a high green density with a polyurethane binder about 2.8% of water in granules is necessary.

Fig. 2 illustrates the dependence of green tensile and flexural strengths in function of binder concentration for samples pressed from granules with about 2.8% of moisture and then dried at 80 °C for 4 h. From Fig. 2 it is seen that polyurethane binder provides remarkably high green strength. The factors responsible for the strength, polymer to polymer and ceramics to polymer interactions will be discussed in next sections. Depending on binder concentration, the tensile and flexural strengths vary between 1.6–7.0 and 2.0–12.7 MPa, respectively. It is observed in the present work that the flexural strength of bars is about 1.7 times greater than the diametral strength for the same binder concentration. Pressed specimens may have very smooth surfaces, which can affect the flexural strength.

Fig. 3 is a dependence of green tensile strength on polyurethane binder content for pellets dried at 80 °C and not dried. The residual moisture was evaluated about 0.3 and 2.7%, respectively. As can be seen the presence of water in pressed samples reduces the mechanical strength. Plasticization by water decreases polymer to ceramics and polymer to polymer interac-

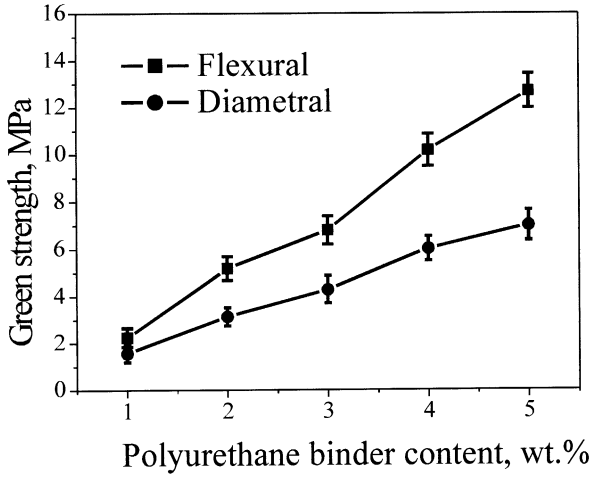

Fig. 2. The tensile and flexural strengths of alumina compacts versus the content of polyurethane binder.

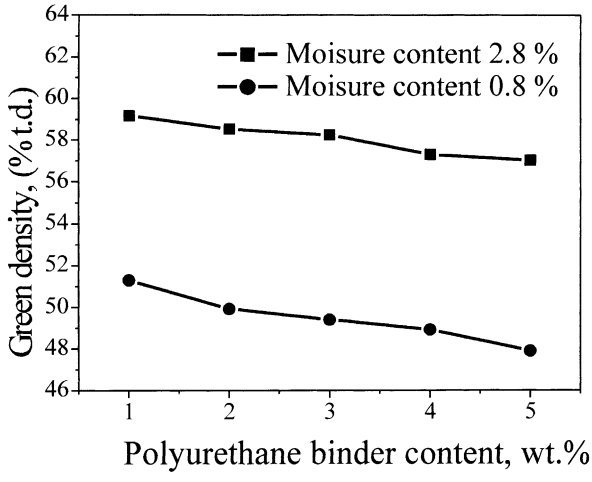

Fig. 1. Dependence of green density on polyurethane binder content.

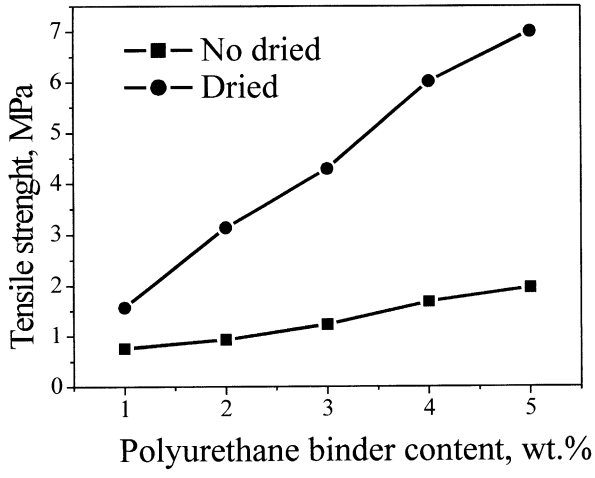

Fig. 3. Variation of tensile strengths for compacts prepared from dried and no dried powders versus polyurethane binder content.

tions. Because T_g of polyurethane binder is 28 °C it ought to be plasticized by water to achieve high green density, but then dried to yield high strength. It arises from Fig. 3 that the moisture effect is greater for greater binder concentration in a pellet. This means that water is mainly absorbed on the polymer phase.

3.2. Results of IR analysis

For explanation of high green strength of alumina compacts with polyurethane binder, IR study was performed to detect the polymer to ceramics interactions. Fig. 4 shows vibration peaks of regions of C=O band and A1–O band of pure polyurethane film, pure alumina powder and alumina–polyurethane composition. In the spectrum of pure polyurethane film, two bands can be seen. The first one at 1744 cm^{-1} caused by the free-of-hydrogen bonding carbonyl vibrations and the second one, at 1710 cm^{-1} caused by hydrogen-bonded carbonyl of urethane groups [15,16]. In the composition spectrum the second band is significally weaker than the first one. It confirms that oxygen atoms of aluminium oxide are competing with –C=O of polyurethane in coordination of hydrogen of urethane groups as is schematically shown in Fig. 5. It signifies that interphacial bond formation between polyurethane binder and alumina powder can be formed and improve polymer to ceramics adhesion.

3.3. Binder burnout characterization

The consecutive criterion in the process of developing a new binder is to determine its thermal decomposition and burnout residue. The burnout characteristic for polyurethane binder was studied by TGA, DTA and pyrolysis of bulk samples. Fig. 6 shows the TGA results of polyurethane binder in air and in nitrogen. In air, the polyurethane binder starts losing its weight at approximately

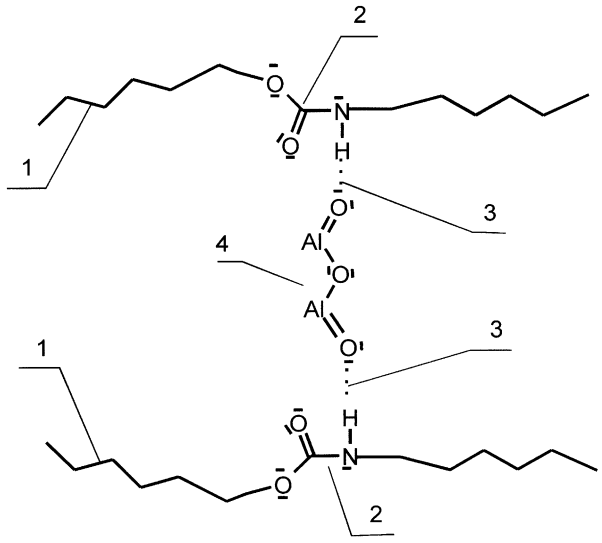

Fig. 5. The schematic representation of particle interactions between polyurethane binder and alumina.

120 °C. Upon reaching 200 °C, the polymer loses about 10% of its weight. This pattern continues to approximately 470 °C where the weight loss reaches 90%. In the range 470–600 °C the weight loss slows down compared to the previous stages. At 600 °C it reaches a plateau, leaving 0.4% residue. This value of residue was determining by pyrolysis of bulk samples to better accuracy. The temperature range of burnout in nitrogen is narrower to that one obtained in air. In nitrogen, the polyurethane binder starts losing weight at approximately 180 °C. Upon reaching 300 °C, the polymer has lost

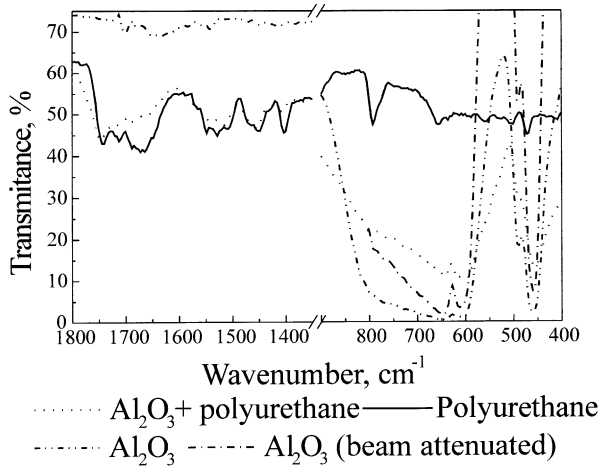

Fig. 4. IR spectra of alumina–polyurethane binder composition compared with spectra of pure alumina and pure polyurethane binder.

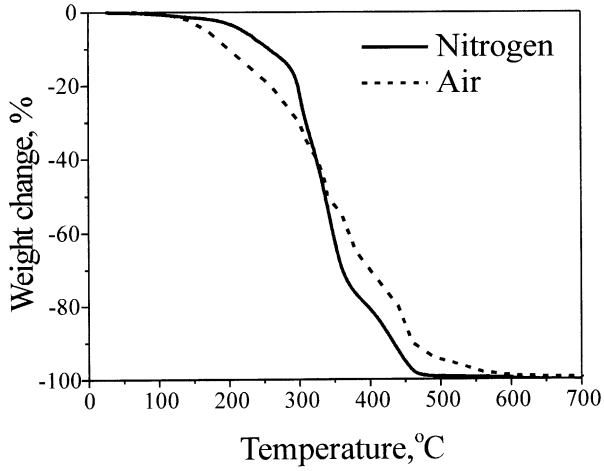

Fig. 6. Thermogravimetric analysis of the polyurethane binder in air and in nitrogen.

about 20% of its weight. Above 300 °C the polymer continuously degrades and at 475 °C the weight loss reaches a plateau, leaving 0.1% residue. The broader temperature range of burnout and more residue in air compared with nitrogen is probably related to a different mechanism of thermal decomposition in oxidizing and inert atmosphere. This is confirmed by DTA results shown in Fig. 7. In nitrogen atmosphere, no exothermic peaks occur in DTA curve suggesting that the polyurethane undergo depolymerization. As can be seen from endothermic peaks of DTA curve in Fig. 7 the thermal decomposition is due to the dissociation of urethane groups in the temperature range 290–380 °C and, later, of ester groups at 400–520 °C [17]. The DTA curve in oxidizing atmosphere has two exothermic peaks in the temperature ranges 350–390 and 460–550 °C. This indicates that thermal decomposition of polyurethane binder is related to oxidation reactions. Polyurethanes are generally composed of hard and soft segments. It has been stated that during thermal decomposition of polyurethanes in air, oxidation reactions of the hard segments occur in a later stage than those of the soft segments [18]. The hard segments of polyurethane binder used in this work are composed mainly of alicyclic rings. Oxidation of hard segments of polyurethane binder causes that the char residue in air is greater than in nitrogen.

The binder burnout characteristics in air and in nitrogen indicate that introducing the polyurethane dispersion during granulation process should not decrease the final density of ceramic parts. Sintering was conducted in 1620 °C during 2 h for samples with 1 and 5 wt.% of polyurethane binder. The final density of samples prepared with 1 and 5 wt.% of polyurethane binder was 97 and 95% t.d., respectively.

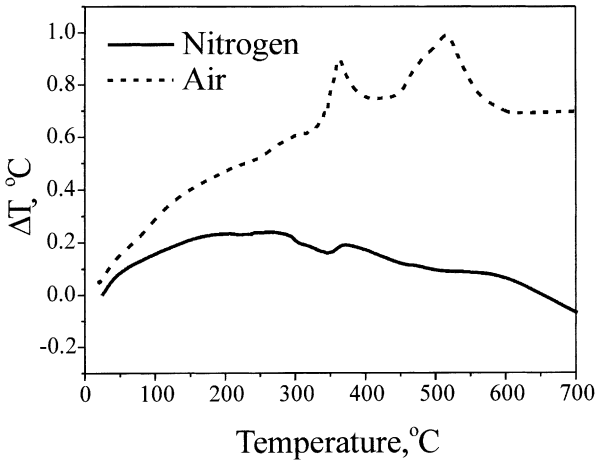

Fig. 7. Differential thermal analysis of the polyurethane binder in air and in nitrogen.

4. Conclusions

1. The polyurethane binder provided high green strength of dry-pressed alumina compacts. Depending on binder concentration (1–5 wt.%) the tensile and flexural strengths varied between 1.6–7.0 and 2.0–12.7 MPa, respectively.
2. IR study revealed that the high green strength was controlled by hydrogen bonding between oxygen atoms of alumina oxide and urethane groups of binder phase.
3. The glass transition temperature of polymer influenced the binder behaviour in the ceramic processing. For decreasing T_g the binder had to be plasticized by water to achieve high green density, but then dried to achieve high green strength.
4. The polyurethane binder had a gradual burnout with a low char residue in both air and nitrogen.

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