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Original Article

Micro extrusion of innovative alumina pastes based on aqueous solvent and eco-friendly binder

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ABSTRACT

The aim of this work is to develop the micro-extrusion process with an innovative approach linked to respect for the principles of green chemistry. Alumina pastes are prepared in an aqueous medium with psyllium as a natural binder, which is not derived from the petrochemical industry. The challenge is to obtain a concentrated system which is suitable for the micro-extrusion process and which ensures satisfactory structural and mechanical properties of the final parts.

The manufacturing of alumina networks is achieved by using the micro-extrusion shaping process consisting of an XYZ displacement platform and a homemade extrusion head. The nozzle diameter is equal to 400 µm. The rheological behavior of the paste is studied as well as its capability to be extruded. The green parts are consolidated by heat treatment at 1600 °C. Their microstructural characteristics have been studied. Final density equal to 98% has been obtained.

1. Introduction

Micro-extrusion is a shaping process which is used to make geometrically complex 3D ceramic green bodies at a micrometric scale [1] from a paste. Ceramic pieces processed with this technique can find a wide range of potential applications in various domains such as health [2,3] and energy [4]. Moreover, micro-extrusion presents a great flexibility because parts can be made tailored to specific shapes thanks a CAD format without requiring further machining or special tools. This process has been developed since the 1990s as reported in papers such as those of Cesarano [5] or Lewis [6]. Advances in research concerning this process are numerous, for example in terms of accuracy of the printed parts, varieties of raw materials used and therefore of formulations (glass [7,8], silicon nitride [9], ceramic precursors of silicon oxycarbide [10]), or of the complexity of fabricated geometries.

The success of this shaping process depends strongly on the rheological behavior and hence on the composition of the used paste. In order to confer suitable rheological behavior to a concentrated ceramic system to extrude a thin section and to ensure a sufficient cohesion to the green part, several additives have to be used (dispersant, plasticizer, binder). These additives come mainly from the petrochemical industry and could potentially have a negative impact on the environment and on the operator's health. With the objective to develop ceramic pieces that meet the criteria of green chemistry, attention should be paid to other types of formulations containing, water and eco-friendly additives. Studies have already been successfully carried out in this direction. For example, pastes or suspensions based on pectin [11] or cellulose derivatives like methylcellulose [12], ethylhydroxyethyl-Cellulose [13] have been reported in the literature. However, since of cellulose is not water-soluble, these cellulose-derivatives are formed by chemical transformations such as substitution of hydroxyl groups by methoxyl groups using caustic soda solution.

To go further, in the context of developing environmentally-friendly processes and possibly in the respect of the development of the principles of green chemistry, a new paste formulation based on psyllium, a natural binder, obtained from plants and not chemically transformed, is described in the present paper.

In this respect, different objectives have to be reached:

(i) to produce a paste with a natural binder, with a high powder (alumina) content,
(ii) to determine its rheological characteristics and to relate them to the feasibility of extrusion through a 400 µm nozzle,
(iii) to consolidate the material and to characterize the microstructure and the mechanical properties of the manufactured parts.

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2. Experimental methods

2.1. Starting raw materials and preparation of the binder

The alumina powder (P172-SB, Alteo, France) used in this work has a specific surface area (B.E.T) of 8 m^2/g, an average particle size (d_{50}) of 0.4 μm. The dispersant is an ammonium polymethacrylate (Darvan C, Vanderbilt) and the lubricant is glycerol, also used as plasticizer.

The binder is a gel made by mixing 5 wt% psyllium powder (Vitacel P95, J. Rettenmaier & Söhne) with demineralized water and then placed in a refrigerator at 8 °C for 20 h before using it for the paste preparation for conservation (as for a foodstuff). More particularly, psyllium is a dietary fiber (Heteropolysaccharide, mainly based on xylose and arabinose) produced from the seed husk of the Indian plant named Plantago Ovata. It consists to 100% of plant based-material and is therefore to 100% natural (no chemically transformations) and appears to be an excellent candidate for use as a natural additive [14]. It has many health benefits, for instance, related to decrease of cholesterol in the body or healthy functioning of the colon [15]. It is used in many food applications to yield a nutritive improvement [16]. These properties are due to its gelling characteristics. Psyllium has indeed an extremely strong water-absorbing ability [15]. In the presence of water, it swells and forms a gel with a pH value close to 7. Mechanisms of this gel formation are well documented in literature [17]. To visualize this phenomenon, observations with an environmental scanning electron microscope (Quanta 450 ESEM FEG, FEI) under controlled humidity of initially dry particles of psyllium were carried out.

2.2. Paste preparation

The different steps of the paste preparation are presented in Fig. 1. Alumina powder was mixed with the dispersant in demineralized water in a planetary mill for 1 h30. Then, the mixture was dried to remove free water. The compact solid obtained is then crushed in a mortar and sieved through a 200 μm mesh to minimize the size of compact agglomerates.

The previously prepared psyllium gel was then introduced at room temperature in a Z-blade mixer with glycerol and dispersed dried alumina. After 1 h30 mixing, the aqueous paste was taken out and placed in the refrigerator at 8 °C for 24 h (Fig. 1).

A formulation, containing 49 vol% alumina was prepared. The glycerol/alumina volume ratio is equal to 14.5%. According to the literature, alumina paste containing around 50% in volume of alumina have indeed been prepared successfully [18].

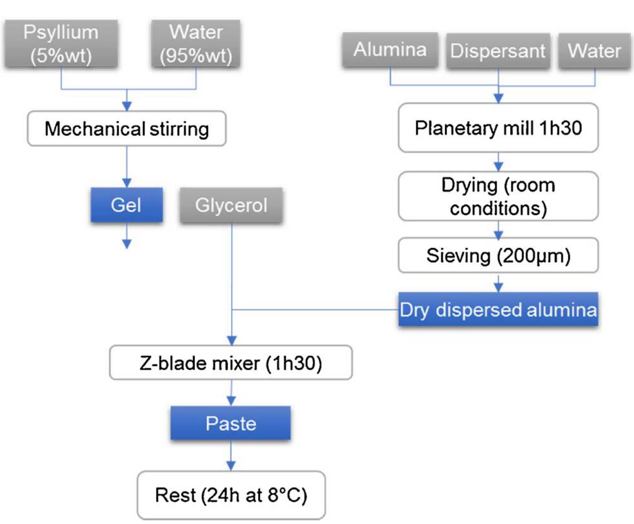

Fig. 1. Paste preparation protocol.

2.3. Rheological behavior of the gel and pastes

The contribution of the gel in the rheological behavior of the pastes has been evaluated. Rheological properties of gel containing up to 3% wt of psyllium were investigated in literature, for instance through the works of Guo [16] or Farahnaky [19]. However, since it is a natural product, differences between psyllium purity, particle size or chemical composition can appear. In this study, a concentration of 5_{wt}% psyllium was chosen in order to make a gel with a high viscosity.

First, the rheological properties of the psyllium gel are measured at 23 °C, 24 h after preparation using a 60 mm diameter cone-and-plate geometry in an ARG2, (TA Instrument) rheometer. The shear rate is increased from 0 to 100 s^{-1} in 60 s, followed by a dwell at 100 s^{-1} during 180 s and finally decreased from 100 to 0 s^{-1} in 60 s. To complete this study and to determine the dynamic viscoelastic properties of the psyllium gel and of the pastes, tests were also performed in oscillations using the same rheometer with a Vane geometry, 24 h after preparation. The linear viscoelastic region (LVER) was determined by oscillatory strain sweep from 0.01% to 1000% at a fixed frequency of 1 Hz.

2.4. Micro-extrusion

The pastes are extruded with a digital controlled device consisting of an XYZ displacement platform and a homemade extrusion head. It is based on a ram extruder. The plunger is motorized by a servo-motor coupled to a gear box. The machine can be programmed with G-code language.

With this head, extrusion at pressures up to 600 bars is possible. The paste is compacted manually inside the barrel whose diameter is equal to 6 mm before extrusion. A constant speed of 8 mm s^{-1} is applied to extrude the paste through a nozzle whose inner diameter is equal to 400 μm. When the paste extrusion need to be discontinued, the motor is stopped and the ram is pulled back to release extra-pressure in the paste. The aim is to avoid a drooling phenomenon as described in literature [16][18]. The shaped geometries are 10 mm long scaffolds with a porous grid-like architecture. The center-to-center distance of the cords is theoretically set to 400 μm (Fig. 2) but dimensional variations could occur during the process. All experiments are performed in an air-conditioned laboratory at an average temperature of 22 °C.

2.5. Debinding and consolidation by heat treatment

After micro-extrusion, alumina green parts are dried during 24 h at room temperature (22 °C, 50% relative humidity) and then heat treated first at 1200 °C for debinding and to consolidation (heating ramp: 5 °C min^{-1}, dwell time: 1 h). After this cycle, the samples are treated at 1600 °C (heating ramp:10 °C min^{-1}, dwell time: 1 h) for further densification.

2.6. Structural and micro-structural characterization

The total pore volume fraction is calculated from both bulk and true density where the true density is measured with a helium pycnometer on dried powder obtained from grinding the sample after heat treatment at 1600 °C in a planetary mill.

The microstructure of sample is studied using an environmental electron microscope (ESEM) to observe the size of the cords after heat treatment, and possible extrusion defects (tearing, sharkskin, porosity, grain size etc.).

2.7. Mechanical characterization of consolidated parts

Finally, the strength of the different extruded pieces is evaluated using a compression test performed with a universal testing machine (Lloyd instruments). Parallelepiped scaffolds with flat surfaces previously polished have been subjected to uniaxial loading using a