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Journal of Materials Processing Technology 169 (2005) 206–213

Journal of Materials Processing Technology

www.elsevier.com/locate/jmatprotec

Rheological characterisation of water-based AlN slurries for the tape casting process

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Received 15 March 2004; received in revised form 30 November 2004; accepted 9 March 2005

Abstract

In the present work rheological properties of aqueous concentrated AlN suspensions have been investigated in the presence of a sintering aid, defflocculant, binder and plasticizers, in order to screen the most suitable experimental conditions to obtain a good rheological behaviour for tape casting thick and non-cracked tapes with good flexibility.

Suspensions exhibiting the desired shear thinning behaviour could be prepared. Adding binder and plasticizers did not change the shear thinning behaviour, but the viscosity revealed an increasing trend with increasing added amounts of binder. The flexibility was improved for the tapes derived from the more viscous suspensions containing higher amounts of binder. Crack free tapes having a maximum thickness of 1.5 mm, and with binder and plasticizer contents in the ranges of 10–15 wt.% and 5–10 wt.%, respectively, could be obtained.

Keywords: Rheology; AlN; Aqueous processing; Tape casting

1. Introduction

Tape casting is a low cost process for making high quality laminated materials for which an adequate thickness control and good surface finish are required. This is one of the most widely used techniques for producing thin ceramic sheets that are subsequently laminated to fabricate products such as capacitors, substrates for integrated circuits for uses in electronic applications [1,2]. In this process, a well-mixed slurry consisting of a suspension of ceramic particles along with other additives, such as dispersants to assure the stabilisation, and binders and plasticizers to confer adequate strength and flexibility to the tape [3–5]. Once the suspension has been prepared it is cast onto a surface through the action of a blade that levels the slurry. The cast is then dried until the solvent has evaporated. The organic components, i.e., binder, plasticizer and dispersant, remain in the tape after casting, but they are generally eliminated by burning them out, thus generating an open porosity in the green body. Obviously, a homogeneous and uniform product can only be obtained if the starting suspension itself has a high homogeneity and stability. This homogeneity must be preserved during all the processing steps of casting, drying, burning out and sintering, and requires a careful selection and accurate control of the processing additives in the slurry.

As in other forming methods, the arrangement and packing of the particles in the green body influences the sintering behaviour and the final properties. The green microstructure depends on the system to be consolidated and the forming technique employed. Assuming well-dispersed starting slurry, the microstructure of the casting tapes will be determined by two key processing factors: (i) particles' arrangement during the casting process and the shrinkage during drying; (ii) the shear stress generated when the slurry passes under the blade. Due to all of these reasons, the rheological behaviour of the suspensions is of paramount importance in the tape casting process. The rheology determines the flow behaviour in the casting unit, which is dependent on the type and concentration of powder, binder, solvent and other organic additives such as dispersants and wetting agents.

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doi:10.1016/j.jmatprotec.2005.03.007

Tape casting has traditionally been performed using organic solvents as dispersing liquid media but there is now a trend to move away from organic solvents and an expected transition towards water-based systems [6–8]. The main advantages for switching from organic to a water-based system are reduced health and environmental hazards coupled with a lower cost. However, the known reactivity of the AlN powders towards water makes the processing of this powder in aqueous media very difficult. Many efforts have been made to protect AlN powders against hydrolysis in order to obtain aqueous suspensions [9–12]. In a previous work, aqueous stable suspensions with 50 vol.% of aluminium nitride have been successfully prepared in the presence of different surface active agents, namely H_3PO_4 and an anionic surfactant having carboxylic functional groups [13].

Nevertheless, the replacement of organic solvents by water has a strong influence on rheological behaviour of slurries due to the poor solvency of water towards organic binders [14]. This replacement also affects the drying behaviour of the tapes and the critical crackling thickness due to the higher surface tension of water that gives rise to the development of stronger capillary forces. A wide range of water soluble binders exists and several of these have been already evaluated for tape casting, including derivates of cellulose ethers such as hydroxyl-ethyl-cellulose, and hydroxyl-propylmethyl-cellulose, polyvinyl alcohols, acrylic polymers, etc. However, water soluble binders tend to increase the viscosity of suspensions and, because of that, the preference usually goes towards acrylic polymer emulsions, more commonly referred as latex binders [4,5,7].

In the present work rheological properties of aqueous AlN suspensions in presence of different amounts of dispersant, binder and plasticizers, have been investigated. The compatibility between binder and plasticizers, in presence of all the components in the formulation of the aqueous AlN suspensions (protective agent, dispersant, sintering additive) was evaluated, by viscosity measurements. Time dependent behaviour was evaluated and dynamic measurements were performed in order to select the most suitable processing conditions like the casting speed for a given tape thickness. Non-cracked green tapes with high thickness and good flexibility could be obtained.

2. Experimental procedure

2.1. Materials

An aluminium nitride powder obtained by self-propagating high temperature synthesis, hereafter designated by AlN-SHS, with a mean particle size of 2.5 μm was used in this work. A commercial polymeric emulsion (MDM2, ÁgoraMat Ldt, Portugal) with a pH value of about 4, was used as binder. It consists of an aqueous dispersion of small polymer particles with a diameter range of 0.3–2 μm, with a solid content of about 53 wt.%. Due to the sufficiently low glass transition temperature of the binder (approximately −10 °C), it is flexible at room temperature. To increase the elasticity of the green tapes, two commercial polymeric products based on polyvinyl alcohol with different average molecular weights, 200 and 400 g mol^{-1} (P200 and P400, ÁgoraMat Ldt, Portugal) were used as plasticizers.

2.2. Preparation and characterisation of the aqueous suspensions

Stable aqueous AlN-SHS suspensions containing 40 and 50 vol.% (95 wt.% AlN-SHS + 5 wt.% CaF_2) solids could be easily prepared following a method described elsewhere [15]. The method comprises the simultaneous adding of 0.4 wt.% H_3PO_4 as a protective agent against hydrolysis, and a suitable amount of a dispersing agent (D), an anionic surface active agent.

Rheological properties of the suspensions were determined using a rotational Rheometer (Bohlin C-VOR Instruments, UK). The measuring configuration adopted was a cone and plate (4°, 40 mm, and gap 150 μm) and stress sweep measurements were conducted between 0.1 and 500 s^{-1}. A first set of rheological measurements (flow curves) was performed using suspensions with 40 vol.% total solids loading dispersed with several amounts of the surface active agent, for a given added amount of binder, in order to gather data about the effect of the added amount of dispersant and select the most appropriate conditions for dispersing the powders' mixture. After determining the required amount of the anionic surface active agent, different proportions of binder and plasticizers 5, 10, and 15 wt.%, based on the mass of inorganic solids, were added and the mixtures let to stir in the polyethylene bottle in a rotating system, for 1 h. The flow curves of the as-obtained suspensions were measured to enable selection of the most appropriate amounts of the processing aids. Based on the experimental results, suspensions containing 50 vol.% solids could be prepared and further characterised concerning time dependent- and viscoelastic-properties.

The time dependent behaviour was evaluated from the recovery time of the viscosity after a steep decrease of the shear rate from 50 (after an equilibration time of 60 s) to 1 s^{-1}. The suspensions were let at this shear rate during 5 min. To evaluate dynamic properties and obtain information on the behaviour of the suspensions in the linear viscoelastic region, stress sweeps with amplitude from 0.01 to 10 Pa at a constant frequency of 1 Hz were performed.

2.3. Preparation and consolidation of the green tapes

The green tapes were prepared by casting the as-prepared suspensions onto a plastic film (Polypropylene (PP) Western Wallis, USA) with a laboratory tape caster (Elmetherm, Oradom Sur Vayres, France). A gap of 2 mm under the blade and a fixed casting speed of ≈3 cm s^{-1} were selected. The processing was carried out at room temperature and humidity. The green tapes were quantitatively characterised by