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Thickness control and interface quality as functions of slurry formulation and casting speed in side-by-side tape casting

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Abstract

A novel method of co-casting called side-by-side tape casting was developed aiming to form thin functionally graded films with varying properties within a single plane. The standard organic-based recipe was optimized to co-cast slurries into thick graded tapes. Performed numerical simulations identified the stable flow beneath the blade with a shear rate profile independent of slurry viscosity as long as the slurry load in the casting tank was low. Thickness and interface shape could be well predicted if the rheological behaviour of slurries is known and the processing parameters are well-controlled. A well-defined steep interface was obtained by co-casting slurries with similar viscosities above 4000 mPas at a speed of 40 cm/min. The elastic properties of green tapes were proven to be defined by the binder concentration in the recipe formulation. The interfaces in graded tapes were shown to withstand high stresses identifying a good adhesion between side-by-side cast materials.

Keywords: Tape casting; Functional graded material; Tape thickness; Rheological properties; Flow behaviour.

1. Introduction

Tape casting is a large scale fabrication technique for flat thin tapes in ceramics, metals and glass processing. The ability to produce uniform tapes tens of metres long which can be subsequently green machined (punched), laminated and stacked to form a specimen with uniform composition and properties, makes tape casting a very versatile manufacturing technique for many products in many industries. Especially, the last decades' technological development requires production of functionally graded materials (*FGM*), meaning materials with a gradual variation in structure and/or composition over its volume and, as consequence, with a gradual change in properties within the sample.[1] Among all ceramic FGMs, recently fabricated by tape casting, multilayer design is the most common to be used in such applications as solid oxide fuel cells (*SOFC*),[2,3] membranes[4,5] and flue gas purification systems.[2] However, in some technologies, planar not layered segmented variation of properties is required. For instance, a planar gradual increase in magnetic phase transition temperature (Curie temperature), greatly improves performance of the active magnetic regenerator (*AMR*) used in the emerging magnetic refrigeration technology.[6,7] This design allows replacement of the expensive rare earth element gadolinium with ceramics as AMR. The requirements are adjacently adhered materials (stripes) varying by a stepwise increase in ceramic doping, forming homogeneous flat dense tapes. To produce such a planar gradual structure (Fig. 1a),[7] the novel shaping technique, so-called side-by-side tape casting (*SBS TC*) also referred to as adjacent tape casting, was proposed.[8]

SBS TC includes simultaneously drawing-out ceramic loaded slurries from the conventional doctor blade tank (tape caster reservoir), which is divided by Teflon partitions into compartments. The number and width of compartments can vary depending on application needs. Under the dragging force of the moving carrier, slurries are co-sheared adjacently forming a

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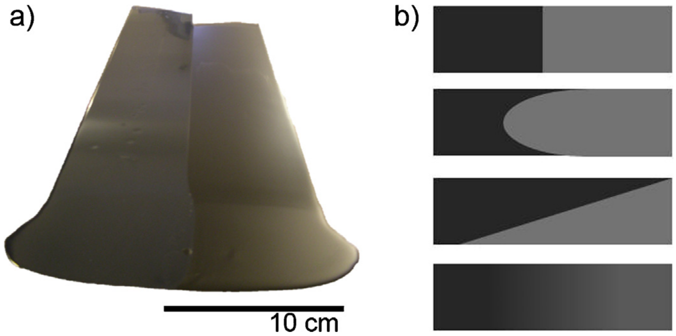

Fig. 1. (a) Photo of a side-by-side (SBS) graded tape with a length of about 40 cm and (b) schematic of possible shapes of interfaces formed between adjacently co-cast materials in SBS TC.

continuous thin tape with one-dimensional interfaces at the confluence areas. In that case, from the tape profile view, interface between SBS co-cast materials (adjacently co-cast materials, stripes) may form one of the following shapes (Fig. 1b): steep vertical, arc shape, angled to the surface of the substrate, or the boundary can be blurred due to mixing and interdiffusion between adjacently co-flowed slurries. The third case is so-called overlapping, which is covering or extending one of the SBS co-cast material beyond another due to the slurries overflow in the interface area.

The challenge of the new adjacent co-casting technique is to produce and maintain the same thickness of adjacent materials having different composition at comparable flow behaviour (similar rheology). Another challenge is the precise control of the interface shape and a sufficient adhesion between the adjacent stripes. In a first optimization of the novel technique, initial parameter settings, such as fluid (i.e., ceramic loaded slurry in current work) properties and processing features are to be determined. This would suggest SBS co-casting of slurries with similar well-studied dispersed phase and use of a well-developed recipe. However, in order to facilitate easier identification and study of the interface area, the adjacent materials are desired to possess solid loads of different compositional, morphological and/or magnetic parameters. Taking these demands into account, the first slurry was formulated based on strontium doped lanthanum manganite oxide $La_{0.85}Sr_{0.15}MnO_3$ (*LSM*), while for the second slurry a mixture of LSM and gadolinium doped cerium oxide $Ce_{0.9}Gd_{0.1}O_2$ (*CGO*) was chosen. LSM and CGO are widely used as cathode and inter-diffusion barrier layer in SOFC, as a solid constitute of the porous layer in gas purification applications and gas separation membranes, LSM perovskite is characterized by high magnetotransport properties and is applied in memory and sensor applications.[9,10] Due to the coarse structure and white colour of the CGO powder, as opposed to the fine rounded shape and black colour of LSM, the interface line between co-cast LSM and mixture of LSM and CGO (*LSM/LSM_CGO*) materials was easily distinguished both visually by colour and due to morphological and compositional differences. Concerning the choice of dispersive media, it was decided to use a well-developed organic-based recipe[2,10] with an azeotropic mixture of methylethylketone and ethanol (*MEKET*) as the solvent. It was important to use MEKET because organic solvents benefit, firstly, in sufficiently fast drying so to avoid inter-diffusion between stripes, and, secondly, minimizing the surface skinning and trapping of evaporating solvent what facilitate better control of the surface finishes. The same MEKET based recipes were applied for both SBS co-cast materials to guarantee similar drying kinetics and shrinkage.

The work addresses the processing approach of adjacently casting LSM and LSM_CGO slurry by the SBS TC technique. For this purpose (i) the influence of the slurry properties (slurry density, rheology, solvent content and loadings of organic additives) and (ii) the casting parameters (speed) on the adjacently graded tape quality were investigated. Specific focus was set on the thickness variation of green tapes and the quality of the interface between the two adjacent stripes.

2. Experimental procedures

2.1. Raw materials and slurry preparation

The SBS cast tapes were prepared by adjacent co-shearing of two slurries. The first slurry initially contained 62.05 wt.% of $La_{0.85}Sr_{0.15}MnO_3$ (LSM, Haldor Topsoe A/S, Denmark; calcined at 1200 °C for 2 h, 18.0 m^2/g, 6.55 g/cm^3). The second slurry had 52.05 wt.% LSM with 5.74 wt.% of $Ce_{0.9}Gd_{0.1}O_2$ (CGO, Rhodia, France; uncalcined, 12 m^2/g, 7.71 g/cm^3) as a solid loading. Slurries were prepared according to standard MEKET (azeotropic mixture of methylethylketone and ethanol) based recipe[2,10] using PVP (polyvinylpyrolidone) as a dispersant.

The preparation of both LSM and LSM_CGO slurries was performed taking into account the necessity to cast highly viscous slurries. In order to achieve homogeneous component distribution and avoid competitive adsorption of polymers in the slurry with a low solvent content, powder and PVP dispersant were dispersed in solvent in two steps. First, 52.05 wt.% of the powder and 0.85 wt.% of the PVP dispersant were milled in the MEKET solvent for about 20 h. The second portion of powder and the remaining 0.21 wt.% of PVP were added whenever the first portion of powder was fully dispersed. The obtained suspension was milled for another 20 h. After adding the binder system (binder polyvinyl butyral PVB, plasticizers dibutyl phthalate DBP, polyethylene glycol PEG, and release and wetting additive with commercial name Additol) in MEKET to the powder and dispersant suspension, the slurry was milled for another 20 h. Finally, d_{50} for both slurries was within 2.3–2.5 μm. Before tape casting, LSM and LSM_CGO slurries were filtered through a 100 μm meshed tulle and the slurries were degassed using a vacuum pump (100 mBar) in order to remove air bubbles.

Particles size distribution was measured during the whole period of the slurry preparation using Scattering Particle Size measurements (Beckman Coulter LS 13320, Beckman Coulter Inc., Miami, FL). The apparent viscosity (η) measurements were conducted on pre-sheared and recovered slurries with reversing increase of shear rate γ' up to 50 s^{-1} using a plate–plate system (Haake RheoStress 600, Thermo Electron GmbH, Karlsruhe, Germany). A solvent trap was used to minimize the evaporation of organic solvent during rheological measurements. Slurry