Tape Casting of Adjacently Graded Materials

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Publication date: 2012

Magnetic refrigeration at room temperature is a developing alternative for conventional vapor compression refrigeration due to lower energy consumption and environmentally friendly materials [1, 2]. For this high efficiency magnetocaloric materials with a graded Curie temperature (T_C) are desired. To achieve that goal, the novel method of simultaneous tape casting of a number of different materials next to each other (Fig. 1) was developed and fundamentally studied. The process comprised modification of doctor blade tank, investigation of slurries rheological behavior, modeling and experimental study of tape casting parameters affecting on casted tape thickness, optimization of de-binder and sintering profiles, detailed exploration of interface area by microscopy, adiabatic temperature change, and analysis of their mechanical properties.

Main task of tape casting is to form composite materials to join target properties of ceramics, metallic particles or glass in one material with clearly specified properties and geometrical parameters. This technique used for a large scale production of thin (from 0.5μm to few mm), uniformly dense or porous, dimensional stable films, which found application in electronics, photonics, fuel cells, technical ceramics and many other emerging technologies. The typical tape caster contains moving conveyor with plastic film on it, fixed casting head (tank) and doctor blade, drying area with controlled ventilation system. In the process slip is poured into tank reservoir and this slurry is then dispensed in the gap between doctor blade and moving plastic carrier, forming a tape with predetermined thickness.

To be able to cast a few slurries adjacently, multi chamber compartment were mounted behind the doctor blade in the casting head. To achieve that, plastic plates have been fabricated by such a way that they completely repeated the shape of the vessel chamber [3]. In addition, a specially designed plastic partition was proven to be sharpen in the corner next to the doctor blade to facilitate smooth co-flow of contiguous slurries. That also prevents rheological instability of slips, improving the tape interface quality.

For fundamental understanding the physics of side-by-side tape casting, two slurries containing La_{0.85}Sr_{0.15}MnO_3 (LSM) and LSM with 10% Ce_{0.9}Gd_{0.1}O_2 (CGO10) materials has been chosen for casting. Adding smaller particles of CGO10 was aimed at detection of the interface area between materials differentiated by a chemical nature of powder, various density and particle size distribution. In order to mountain sintered tape in the prototype of active magnetic regenerator, production of several ~300 μm thin graded plates of the magnetocaloric material was required. Considering drying and sintering shrinkage, 1mm gap was chosen.

The common tape casting involves the use of two doctor blades. While first doctor blade “shears” a slurry, the second one situated behind is intended to control the slurry level, keeping hydrostatic pressure in the space between two doctor blades to be constant. This results in formation of smooth uniformly thick tape. Developing a novel side-by-side tape casting method, it became evident that the usage of two doctor blades makes design more complicated and inaccurate [3]. On the other hand, the thickness of the tape casted by one doctor blade dramatically depends on both the pressure exerted by the slurry column in reservoir and the velocity created by moving substrate. Good agreement was found between experimental tape casting of single material and modeling data. The simulations helped to understand the correlation between tape thickness (δ) and substrate velocity (v₀), initial height of
slurry in the vessel \( (H) \) and the height of doctor blade itself \( (h) \) [4]. The slurry flow under the doctor blade was described by a simple quasi-steady momentum equation in combination with an Ostwald power law constitutive equation. It was integrated in to a closed form analytical solution for the dried green tape’s thickness. Based on this research it was proved that tape casting with higher velocity leads to more uniform but thinner tape formation. Making process slower leads to thicker plate generation, but the drying process in that case is more controlled. By increasing carrier speed, tape’s thickness decreases hyperbolically. It was observed that the height of tape at the end point of the stripe is greater than that at the beginning of the stripe. Moreover, by increasing the material load (the height of slurry in the reservoir) the aforementioned differences between the beginning and the end of tape is raised. Taking it into consideration, during the rest of experiments the casting speed, \( v_0 \), was fixed at 22cm/min, giving shear rate of \( \dot{\gamma} \) 3, 67 s\(^{-1}\) using 1mm gap.

As rheological behavior and density of slurry assumed to have the largest effect on the quality of casted material, viscosity values were intended to vary in the wide range. All slurries were characterized by shear thinning effect (as required for tape casting) what can be caused by alignment of particles and/or polymers chain stretching in the direction of casting. Both of these processes decrease suspension viscosity. Besides, oscillation test indicated that suspensions were not prone to sedimentation during storage, and that the liquid component prevailed over the viscous for a whole interval of shear stress applied in casting. It was unveiled that side-by-side tape casting is possible to use for slurries with viscosities in the range of 4000 to 6000 mPas at a shear rate 4s\(^{-1}\). Solvent evaporation in vacuum was conducted in order to evaluate drying kinetics and to control the slurry viscosity before tape casting implemented. Experiments proved that viscosity and mass loss increased logarithmically with time [5].

Although sintering process is the last one on the path of final material manufacturing, it is the stage in which minor defects emerge, resulting crack formation and distortion. Performed with different heating rates thermogravimetric (TGA) and differential thermal analysis (DTA), identified the temperatures of 200 and 400°C as organics decomposition ones at the optimum of 5°C/min heating. To upscale the data, which were measured with TGA and DTA, burnout and sintering profile were reproduced on TOMMI optical dilatometer. This technique revealed the heating profile of 0.3°C/min to 400°C and after to 600°C with a 2h’ dwell time for each of above mentioned temperatures provided optimal conditions for organic additives burnout. Sintering process was completed at 1275°C for 4h with heating rate of 0.3°C/min and cooling to room temperature of 1°C/min [5]. From the optical dilatometry test, it also can be concluded that the shrinking behaviour of interface area is dominated by the material, which shrinks to the higher extent. This phenomenon can be explained by the physics of stress development and densification during sintering.

In order to examine further the interface area and the magnetic properties of the side-by-side casted tape, energy dispersive X-ray (EDS) mapping and adiabatic temperature change were analyzed. In practical sense graded material with 5 stripes of \( \text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{Mn}_{1.05}\text{O}_3 \) (\( x = 0.03–0.09 \)) (LCSM) compositions were interesting [3]. Despite of stripes were diverged only by stoichiometry of mixed valence manganese ceramics, the interface areas were easily identified by microscopy due to different tapes density. EDS mapping confirmed the location and shapes of interfaces. The adiabatic temperature change of 5 adjacent materials showed continuously increasing Curie temperature value required for the application. Sample of two contiguous stripes were also tested on the magnetic refrigerator prototype built in Technical University of Denmark [6, 7] and performed a large temperature span of 9.3K as an active magnetic regenerator [8].

In the present work, the novel method of adjacently casted ceramics was thoroughly investigated with focus on exploration of interfaces between stripes. In order to achieve necessary magnetic
properties, the border in the transition region was required to be well defined. The objective of this work was to predict morphological, mechanical and magnetic properties of post-sintering tapes assigned the initial production settings, i.e. slurry compositions and rheological characteristics as well as tape casting and sintering parameters. Taking into consideration that the ultimate goal was both to improve the side-by-side tape casting processing and to investigate magnetic properties of the targeted materials, tape caster was modified and slurry properties were adjusted. Developed method of new design of ceramic materials can be easily scaled to industrial mass production or expand the application area for that class of materials.

Fig. 1. Adjacently casted tape.

4. M. Jabbari, R. Bulatova, J. H. Hattel, and C. R. H. Bahl, Quasi-Steady State Power Law Model for the Flow of La0.85Sr0.15MnO3 Ceramic Slurry in Tape Casting (under reviewing).