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THE VARIATION OF INTERFACE FORMATION WITH THE SLURRY VISCOSITY CHANGE IN SIDE-BY-SIDE TAPE CASTING

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Summary

Homogenous and flexible adjacently graded tapes were produced by casting the organic-based slurries simultaneously. To develop side-by-side tape casing (SBSTC), the material optimization, modernization of the doctor blade design, and parameters control of such processes as casting, drying, de-bindering and sintering were studied. Solvent and binder concentrations were varied in order to optimize co-casting flow, as well as the drying and sintering shrinkage. Tapes were evaluated in terms of rheological behavior of the slurries, the green and sintered tape microstructure, the quality of the interface area, and the mechanical properties of the green tapes.
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Introduction

Magnetic refrigeration (MR) 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 application, high efficiency magnetocaloric materials with a graded Curie temperature are desired. The functional ceramics with the continuously variable composition and the transition temperature has been recently produced by side-by-side tape casting (SBSTC) [3, 4], resulting in new advanced technique to form thin ceramic plates with adjacently graded materials. One of the main scientific challenges of the graded materials produced by tape casting is to control the interface between the adjacent fluids.

The goal of this work is a deep research of SBSTC with the main focus on the fundamental understanding of controlling of the well-defined and steep interface between the adjacent slurries. For this purpose, a graded tape (**LSM_CGO**) with the solid loadings of $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3/Ce_{0.9}Gd_{0.1}O_2$ (**LSM** and **LSM/CGO**) were used for the first and the second stripes, consequently. In this work, CGO was added into the second slurry in order to form well distinguished interface in between co-casted materials. With the overall aim of developing the SBSTC process, a number of experiments were carried out. The other objective of this work is to predict morphological and mechanical properties of the green tapes given the initial production conditions, i.e. slurry compositions and rheological characteristics.

As mentioned earlier, the main part of this work is to study the multiple material flows. The rheological behavior of the slurries influences not only the entry flow of the multiple materials, but also the homogeneity and stability of the suspensions. Moreover, it results in developing a stress in the contact area while drying, de-bindering, and sintering. Taking all these factors into account, slurries with different viscosity values (achieved by using different ratios between components) have been tape cast. As a result, formation of different interface shapes lead to variations in the shrinkage behavior.

Additionally to the standard procedure, SBSTC technique requires modernization of the doctor blade design. To form well adhered interconnected interface, each individual partition, dividing doctor blade reservoir into smaller vessels, have to be sharpened in the front side [3]. The main challenge of SBSTC is to acuminate partition by a way to let adjacent slurries join and co-flow smoothly, and, as a consequence, without intermixing or leaving partition trace in the interface area.

Experimental

Based on the well-known industrially used recipes [5], the slurries, initially containing of 14,02 vol% $La_{0.85}Sr_{0.15}MnO_3$ (LSM, calcined at 1000°C) and 11,15 vol% LSM with 1,05 vol% of uncalcined $Ce_{0.9}Gd_{0.1}O_2$ (LSM/CGO) were prepared.

To insure a stable slurry, the powder was added in two steps: The 80% of the LSM powder was suspended in MEKET with PVP dispersant and ball milled for 72 h. CGO, if any, and the last 20% of the LSM with PVP as dispersant, was then added to the suspension; and the slurry was milled for further 72 h. Powder, MEKET solvent and PVP dispersant were milled in two steps until the powder is fully dispersed, with the average particle size of 3 µm for both slurries and no further reduction of the particle size was observed. After adding binder solution (binder B60H, plasticizers DBP, PEG, and Additol), suspension was milled for another 24 h. To study kinetics of milling, particle size distribution was measured during the whole period of the slurry preparation using Scattering Particle Size measurements (Beckman Coulter LS 13320 with a measurement range of 0.04–2000 µm, Miami, FL). All slurries were characterized by a pseudoplastic behavior (viscosity curves are not shown here) as it is required for tape casting.

For the first screening, binder solution and solvent concentrations were varied with subsequent casting and sintering to observe the effect not just on rheological behavior, but also on microstructure formation. After milling and before casting, the slurries were filtered on a 100 µm mesh (thin tulle) to ensure a structure with a powder fine. Then suspensions were degassed in vacuum in order to avoid bubbles in the slurry volume, and to minimize the defects formation during drying process.

The doctor blade was prepared by splitting the loading reservoir into two compartments. The splitting was done with the camper partition [3]. Tapes with the sintered thickness of 300µm were required [4]. To achieve that, the high of doctor blade was adjusted to 1 mm, and tapes were formed with 20 cm/min casting speed. The slurry couples were simultaneously added to each compartment of the doctor blade. After drying, the tapes were punched out and sintered at 1250°C for 4h.

Post sintered tapes were embedded in epoxy, grinded and the cross sections with interfaces were investigated. To study the interface between the adjacent materials in the green state, a cross section of green tapes was prepared and studied with a scanning electron microscope (SEM) (Zeiss, EVO 60 at 15kV with Noran EDS).

For measurement of tensile stress (strain-stress resistivity), samples were fixed in Instron tensile machine keeper providing independent conditions.

Results and discussion

The special procedure of ball milling was used due to necessity to work with slurries of high viscosities (2000 mPa·s to 8000 mPa·s at casting shear rate 4 s^{-1}) while producing adjacently graded tape (Fig.1). Fig. 2 shows decreasing of particles size distribution with milling LSM_CGO slurry, with the casting viscosity of 3000 mPa·s at casting shear rate. The same tendency was observed for all used slips.

The main target of ball milling is to ensure in isotropic reproducible dimensional stability of final tape properties. The high viscosity was achieved by decreasing the amount of the solvent, therefore, milling and mixing was hindered. To achieve a fine microstructure of the cast tapes, solid phase was added in two steps. First, the solvent, dispersant and 80 wt% of the powder were mixed. Once this suspension became less viscous and the smallest particle size was achieved, next 20 wt% of powder was added. On that stage one can see a little jump on the curve, which is due to the addition of the bigger particles to the milled mixture with the finer ones. After this portion of powder was broke down, the third stage of chemicals, such as binder and plasticizers solution, were added. To prevent matrix formation, re-agglomeration of particles, and slurry thickening, 20 hours of milling after binder addition was required.

One of the key factors, influencing the interface shape and position of adjacent tapes, is the slurries viscosity which will be described here in details. To detect the influence of the solvent and binder content on the tape structure formation, two simultaneous experiments were conducted. The first experiment implied solvent content variation, which was proved to have stronger effect on the slurries viscosities, while small variations in binder concentrations had a high impact on tape densification and adherence between the adjacent strips. The majority of the matrix instabilities in the form of the pores and cracks appear throughout the drying process due to the binder lack, while binder excess leads to tape deformations during de-bindering. The biggest challenge of necessity of matching the properties for the co-casted components, especially during densification, was overcome by using the same organic systems for the adjacent materials as well as varying the solvent and binder concentrations in a narrow area of 5 wt% maximum for both ingredients. Four samples with different binder/powder ratio were tested and investigated on a sense of interface area quality (Fig. 3).

Adjacent tape casting, in addition to the possibility of creating sheets of desired thickness and density, aims overlapping and interface position control. Here overlapping is either overflow of one slurry on top of neighboring one, or it's displacement what result to the interface shifting and/or inclination. Fig. 4 shows that beginning of green tape is thicker comparing with end of the cast tapes, no matter which slurry viscosities were used. The changes in the tape thickness are predictable due to constant decrease in

hydrostatic pressure behind the doctor blade region [6]. However, after the first 10 cm the thickness of the graded tapes become more uniform. Moreover, the more viscous slurry is cast, the smoother the tape was produced. Due to the variation of the side flow based on the viscosity of the slurry, the thickness and the width of the tapes uncontrollably vary along the length. More viscous slurries keep the shape stronger, reducing the side flow, and hence the tape thickness becomes more uniform. However, impact of the viscosity on the green tape density is not that strong as on the tape thickness (Fig. 5). That advance one-doctor blade technique for industrial production.
With advantages of adjacently graded tapes properties, the process should comprise formation of steep and flat interface formation. Fig. 6 shows continuous decrease in the overlapping along the tape length. That effect attributes to sharp processing start, due to that overlapping on the beginning of the tape is higher. Co-casting of similarly high viscous slurries leads to formation of steep interface with comparably small overlapping.
To evaluate the SBSTC further in the interface area, the energy dispersive X-ray (EDS) mapping has been carried out. The EDS analysis was performed to compare the composition in the area of the pure material and in the interface region. Unified behavior for the whole range of slurries viscosities with the only difference in overlapping value was observed. No diffusion or intermix between co-casted materials was found. The overlap between the two materials at the interface was less than 600 µm (Fig.7).
Magnetic cooling application requires for the magnetocaloric materials to be able to withstand the heat exchange while the liquid is pumped through graded plates. And to insure in nonablative system, the tensile test was chosen to evaluate the green tapes. Polymers influence on the flexibility and the green strength for the cast tapes, as a result, mechanical properties of pure LSM_CGO green tapes were increasing with loading binder solution and increasing of viscosity, consequently (Fig. 8b). The same tendency was observed for the graded tape, as pure LSM stripe remain constant from sample to sample (Fig. 8a). Therefore, adherence between the co-casted materials improves with increasing of the polymer content.
After tape casting, sheets were subjected to thermo-treatment including burnout and sintering. The heating regime was optimized based on TGA and DTA data (not shown here). Samples were heated up to burn-out temperatures of 200 and 400 °C with 0,5 °C/min heating speed and 2 hours dwell time. Further tapes were heated up to sintering temperature of 1250 °C following by cooling with 1°C/min speed. No any damages or distortion were observed.

Conclusion

Modifying doctor blade reservoir and optimizing slips recipe generates the new design of the cast tapes generation, namely formation of adjacently graded materials different natures, what could be considered for a wide variety applications. The parametric study of SBSTC has been conducted to see how slurries viscosities influence on interface formation. The co-casted green tapes were characterized by uniform density, dimensional stability after 10 cm of cast tape, sufficient flexibility for tapes handling and machining, high strength in green state, absence of defects after de-bindering and sintering. It was shown that the adjacent co-casting of slurries with viscosities higher than 4000 mPa·s leads to the flat interface. Moreover, the more viscous slurries were used, the more uniform tapes with not significant overlapping were achieved.
For the future work, SBSTC with a constant slurry loading in reservoir is planned. That will decrease the tape thickness instabilities. Moreover, experiments with various casting speed will be carried out.

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