INVESTIGATION THE DRYING BEHAVIOR OF CERAMIC SUSPENSION DROPLETS

Aylin ŞAKAR-DELİORMANLI[*1], Erdal ÇELİK[2], Mehmet POLAT[1]

[1] *Izmir Institute of Technology, Chemical Engineering Department, Urla, Izmir,Turkey*
[2] *Dokuz Eylul University, Metallurgy and Materials Engineering Department, Izmir, Turkey*

ABSTRACT

Drying is a major issue in wet processing ceramics. It has crucial effects on the final properties ceramics films especially produced by aqueous based tape casting. In this study structural evolution of ceramic suspension droplets were investigated during drying. Effect of binder concentration on the ring formation from droplets was tested. Results revealed that PMN:latex ratio have some influence on the particle migration and at high latex concentrations particle clusters were observed in the supersaturated region.

Keywords: Drying, tape casting, ceramic suspensions

1. INTRODUCTION

Tape casting is a shaping method to produce two-dimensional thin ceramic plates usually have 10–1000 μm thickness [1]. A paste-like suspension consisting of powder, solvent, dispersant, binder and plasticizer is cast onto a substrate by a moving blade. The final dried green tape should be flexible, and easy to handle [2]. However, drying of ceramic films is a complex process. After casting, the film is in a supersaturated state which means that there is excess water between the particles. Therefore, ceramic particles move freely in the liquid under the influence of the Brownian motion and capillary flow. As the evaporation starts the solids loading of the film increases and it continuous until a particle of network forms that can support the capillary tension created by the liquid. As the evaporation proceeds large pores drain first from the particle network followed by the smaller pores. Further evaporation causes a pendular state and water removal occurs by gas phase diffusion within the internal pores [3-6].

In general, drying can be divided into three stages: constant-rate period (CRP), first fallingrate period (FRP1), and second falling-rate period (FRP2). The first stage of drying is called the constant rate period, because the rate of evaporation is independent of time [4]. In this stage the drying rate is controlled by external conditions. As drying proceeds, large pores drain as fluid is drawn to smaller pores with higher suction potential. The drained pores may penetrate more into the materials interior. The transition to the FRP1 occurs when fluid can no longer be supplied to the external surface at a rate equivalent to the evaporation rate. In the latter stages a transition occurs to FRP2. In this period the remaining liquid is removed by vapor-phase diffusion [4, 6, 7]. The aim of the current study is to investigate the drying behavior of aqueous ceramic suspensions prepared for the tape casting process. In the study effect of binder concentration on the structural evolution of the ceramic suspension droplets were observed during drying.

2. EXPERIMENTAL

2.1. Materials

Lead magnesium niobate powder (average particle size, d50, 1.8 µm and BET surface area of 1.168 m2/g) was produced by combustion spray pyrolysis provided by the Praxair Inc. USA. PAA/PEO comb polymer (PAA 5000 g/mol, PEO 2000 g/mol) was employed as the dispersant to prepare highly concentrated stable PMN suspensions. The binder used in the study was an aqueous based nonionic acylic latex emulsion, Rhoplex B-60A (Rohm and Haas Co, Philadelphia, PA). In the study hydroxypropyl methycellulose (Methocel F4M, DOW Chemicals Co., Midland MI) with a molecular weight of 3500 g/mol was used as the wetting agent.

2.2 Method

Suspensions having different powder/binder ratio and fix hydroxypropyl methylcellulose content were prepared by a multi-step process. In the first step of slurry preparation, highly concentrated PMN suspensions were prepared using PAA/PEO comb polymer. Suspensions were ball milled for 24 hours to ensure complete adsorption of PAA/PEO onto powder surface at pH 9. In the next step latex binder and wetting agent were added to the system and the slurry was ball milled 24 hours more. Details about the PMN slurry preparation for tape casting can be found elsewhere [8, 9].

Table 1. Formulations of the suspensions used in the study [8, 9].

	R1	R2	R3
	wt %	wt %	wt %
PMN	69.60	77.35	80.33
Binder	9.72	5.40	3.74
PAA/PEO(2000)	0.12	0.14	0.14
H_2O	20.46	17.03	15.71
Wetting agent	0.10	0.08	0.08
Total	**100**	**100**	**100**

To investigate the structural evolution of the PMN suspensions during drying concentrated suspensions were diluted to φ: 0.001 and observed under an optical microscope (Olympus IX71, UTVO.5XC.3). For this purpose a 4 µl drop of suspension was put on a cover slide and was allowed to dry under ambient conditions (22 ºC and 36% relative humidity). Images of the micro-drop were recorded using a digital camera.

3. RESULTS AND DISCUSSION

Structural evolution of the concentrated tape casting suspensions is difficult to observe whereas one can analyze the structural evolution of the dilute droplets. This investigation can give some information about the powder-binder interaction during drying period. Upon drying a droplet of liquid typically leaves a ring of solute on the substrate on which it rested [10]. In the current study to investigate the structural evolution of PMN suspensions during drying, samples were diluted to φ=0.001 and observed under an inverted optical microscope as a function of time. The results reveal that the formation of a dense particle layer at the µ-drop perimeter, as drying proceeds (see Figure 1). Figure 2 shows the schematic illustration that identifies the regions in optical icroscope. According to the Fig. 3 cluster formation was not observed in the droplets deposited from the pure PMN suspensions in absence of binder and wetting agent. As expected there is an increase on the thickness of the ring as the drying time proceeds. Complete drying period for the droplet was 44 minutes. Similarly, Figure 4 describes the images of the tape casting suspensions prepared from recipe R1. In the later stage of the drying process, particle clusters were observed in the supersaturated region. Particles also migrated to the edge of the droplet. Furthermore, some flocculation behavior was observed between the particles in the center of the droplet. Similar behavior was noticed in the suspension prepared from recipe R2 (Figure 5). On the other hand, cluster formation was not observed in the droplets deposited from the PMN suspensions prepared from R3 (Figure 6) or pure latex emulsions. Results also revealed that total evaporation time of the PMN suspension droplets changes depending on the PMN:latex ratio. A decrease was observed in total evaporation period from 48 minutes to 38 minutes as the binder concentration decrease.

Figure 1. Schematic presentation of the method followed in the droplet drying experiments from ref. [12].

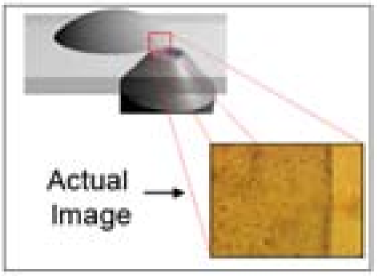

Figure 2. Schematic illustration that identifies the regions in optical microscope images [12].

Ring formation due to drying of droplet is caused by evaporation driven flow [10]. The streaming of the particles from the center of the drop to the edge is due to the geometry of the drop. Because the contact line of the drop has to flow the interface in order to prevent the shrinkage of the drop. The resulting capillary flow drives the particles from the center to the edge of the drop. As a result particle network forms on the contact line. Therefore, when drying is completed most of the solid phase is deposited at the edge [11]. A possible explanation for the flocculation behavior observed in the droplet can be the PMNbinder interactions. Previously, Martinez and Lewis investigated the structural evolution of the alumina: latex system with the same method followed in the current study and they obtained similar results for the alumina: anionic latex system. However, they did not explain the reason that drives the flocculation [12, 13].

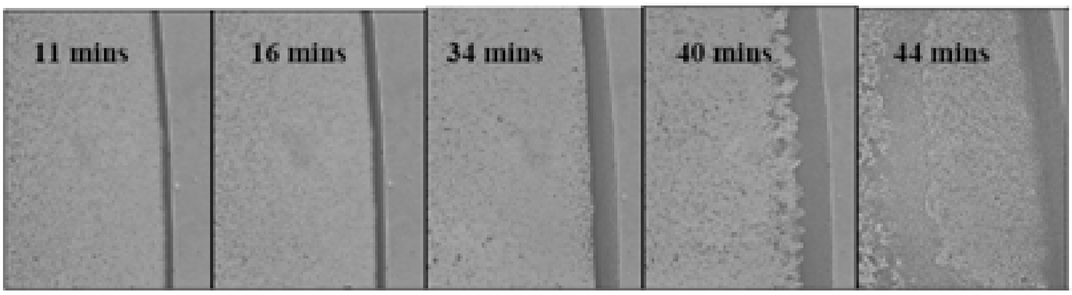

Figure 3. Optical microscope images showing the drying of a droplet contains only PMN particles as a function of drying time.

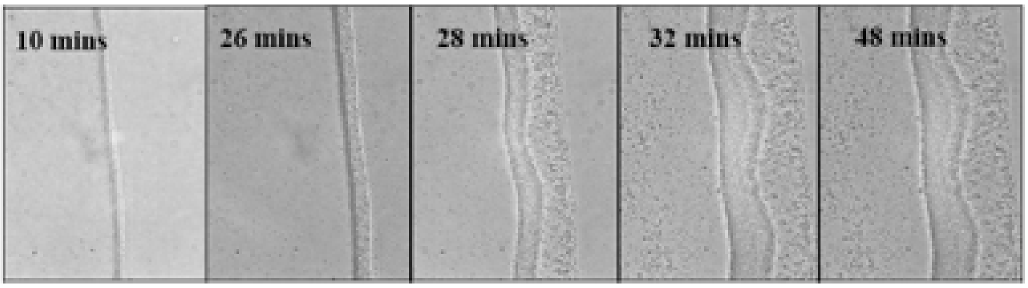

Figure 4. Optical microscope images that show the drying of a droplet having a composition of R1.

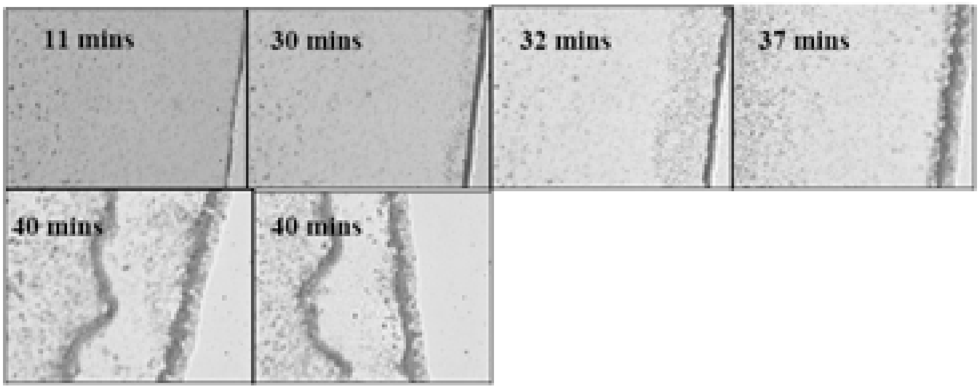

Figure 5. Optical microscope images of a droplet having composition of R2 as a function of drying time.

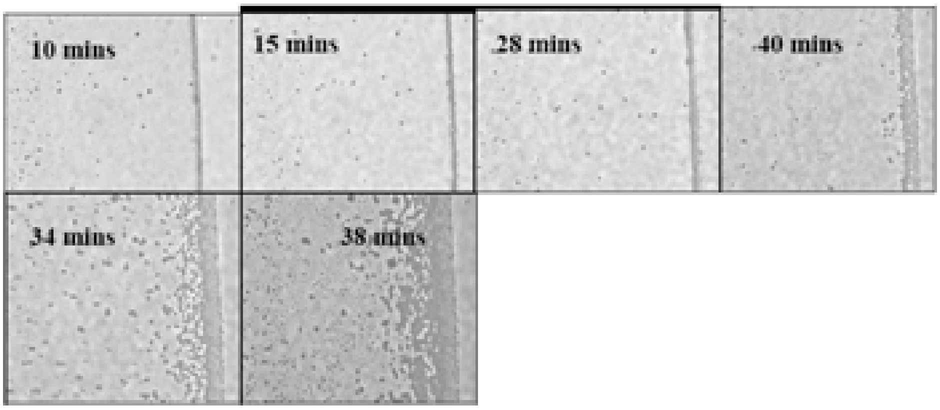

Figure 6. Optical microscope images of the droplet having composition of R3 as a function of drying time.

To summarize, Figure 7 shows schematically the structural evolution of the liquid droplets during drying. Hu and Larson [10] analyzed the evaporation of a sessile droplet. Accordingly, droplet evaporation occurs in two stages. In the first stage, contact line is pinned and the contact angle decreases during drying. As drying progresses particles move to the drop edge under the influence of capillary flow, resulting in the formation of a ring of particles. If evaporation of liquid from the pores is exposing to the solid phase, a solid/liquid interface can be replaced by a more energetic solid/vapor interface. To prevent such an increase in the energy the liquid tends to spread from the interior. Since the volume of the liquid has been reduced by evaporation the meniscus becomes curved. When contact angle reaches a critical value the contact line starts to change. Finally, when the solvent has evaporated the resulting structure is a ring [10-13].

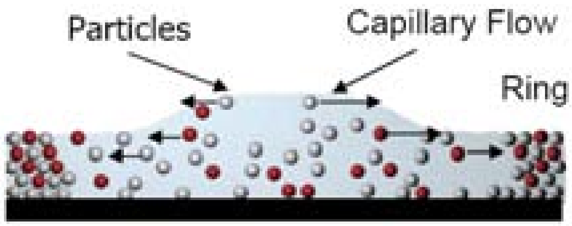

Figure 7. Schematic presentation of the ring formation during drying of a droplet [12].

4. CONCLUSIONS

In the current study structural evolution of PMN suspensions during drying, were observed under an inverted optical microscope. The results revealed that the formation of a dense particle layer at the μ-drop perimeter, as drying proceeds. For the suspensions prepared from recipe R1 and R2 some flocculation behavior was observed between the particles in the center of the droplet. On the other hand, cluster formation was not observed in the droplets deposited from the pure PMN suspensions in absence of latex binder. Ring formation due to drying of droplet was attributed to the evaporation driven flow. The streaming of the particles from the center of the drop to the edge is due to the geometry of the drop.

ACKNOWLEDGEMENTS

Authors would like to thank Prof.Dr.Jennifer A.Lewis, for use of the laboratory facilities at University of Illinois at Urbana Champaign, USA. The project is supported by The Scientific and Technological Research Council of Turkey.

REFERENCES

1. Meier, P.L., Urech L., and Gauckler, L.J., Tape Casting of Nanocrystallize Ceria Gadolinia Powder, Journal of the European Ceramic Society, Vol. 24, No.15, Pages 3753-3758, 2004.
2. Mistler, R.E., Tape Casting: Past, Present, Potential, American Ceramic Society Bulletin, Vol.77, No.10, Pages 82-86, 1998. .
3. Chiu, R.C. and Cima, M.J., Drying of Granular Ceramic Films: II, Drying Stress, Saturation Uniformity, Journal of the American Ceramic Society, Vol. 76, Pages 2769-2777, 1993.
4. Scherer, G.W., Theory of Drying, Journal of the American Ceramic Society, Vol. 73, No.1, Pages 3-14, 1990.
5. Scherer, G.W., Aging and Drying of Gels, Journal of Non-Crystalline Solids, Vol. 100, Pages 77-92, 1988.
6. Rahaman, M.N., Ceramic Processing and Sintering, (Marcel Dekker Inc., USA), 1995.
7. Lewis, J.A., Colloidal Processing of Ceramics, Journal of the American Ceramic Society, Vol. 83, No.10, Pages 2341-59, 2000.
8. Şakar-Deliormanlı, A., Çelik,E., and Polat, M., Thermal Analysis and Microstructural Characterization of Ceramic Green Tapes Prepared by Aqueous Tape Casting, Journal of Thermal Analysis and Calorimetry, (In press).
9. Şakar-Deliormanlı, A., Çelik,E., and Polat, M., Preparation of the Pb(Mg1/3Nb2/3)O3 Films by Aqueous Tape Casting, Journal of the European Ceramic Society, (In press).
10. Hu, H., and Larson, R.G., Analysis of the Microfluid Flow in an Evaporating Sessile Droplet, Langmuir, Vol. 21, Pages 3963-3971, 2005.
11. Deegan, R.D., Bakajin, O., Dupont, T.F., Huber, G., Nagel, S.R., and Witten, T.A., Capillary Flow as the Cause of Ring Strains from Dried Liquid Drops, Nature, Vol. 389, Pages 827-829, 1997.
12. Martinez, C.J., Structure and Property Evolution during Film Formation from Binary Colloidal Suspensions, PhD Thesis, University of Illinois at Urbana Champaign, 2002.
13. Martinez, C.J., and Lewis, J., Rheological, Structural, and Stress Evolution of Aqueous Al2O3: Latex Tape Cast Layers, Journal of the American Ceramic Society, Vol. 85, No.10, Pages 2409-16, 2002.