

Drying Phenomena during the formation of particulate films from colloidal suspension

S. Inasawa and Y. Yamaguchi

Department of Chemical System Engineering
The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-8656, Japan

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1. Introduction

Coating and drying of colloidal suspension on a substrate is a practical way to form colloidal films. One of the expected applications of these colloidal films is photonic crystals and much attention has been paid to how to obtain well-ordered colloidal films from wet processes. As evaporation of solvent proceeds, suspended colloidal particles are concentrated and finally “precipitate”. One important difference between conventional continuous thin films and particulate films is that the latter contains a lot of voids or pores after film formation. Because of the geometric restriction, the maximum volume fraction of spherical particles in a film is 0.74 at most when they are in hexagonal close-packed structure. The rest is vacant void and we have many small spaces between particles. Especially, in particulate films which consist of spherical particles with a diameter of submicron or less, vacant space is nanometer scale and solvent tend to flow into the film to wet particles because of a large capillary force^[1]. This results in an additional flow of solvent during drying. Thus, unlike general continuous film coating, drying process of colloidal suspension is affected by the formed particulate films, which makes drying phenomenon more complicated.

Drying of colloidal suspension is widely studied so far, such as consolidation of suspended particles^[1,2], drying dynamics of a colloidal suspension^[1,3] and air invasion into packed particles at the last stage of drying^[4]. Among them, crack formation mechanism is a practical subject in this field because cracks degrade the quality of the film and is not preferred. Cracks are formed when solvent between packed particles is replaced with air and the consolidated particulate film shrinks. This shrink is caused by strong capillary force that acts on individual particles^[1]. The capillary force is expressed by a simple equation,

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$$\Delta P = \frac{2\gamma}{r} \quad (1)$$

where γ is the interfacial energy between air and solvent and r is the curvature radius of the meniscus between particles. Because the curvature radius r becomes small when we use small colloidal particles, particle radius is one of the decisive factors for crack formation.

Another interesting feature of crack formation in particulate films is that cracks frequently occur along drying direction of the films^[5-7]. Sometimes, formed cracks show periodic patterns^[1,5,6]. We found the formation of cracks that are perpendicular to the drying direction. This unique “lateral” crack formation was observed only when we used small colloidal particles with a diameter of ca. 10 nm. Drying of colloidal suspension with larger particles does not give us such a unique phenomenon. Furthermore, lateral crack spacing clearly depends on drying temperature. In our talk, a detailed description of the lateral cracking phenomenon and possible physical mechanism is discussed.

2. Experimental

Colloidal silica particles dispersed in water was used for film formation. The average diameter of silica colloids is ca. 10 nm. For particulate film formation, we used a handmade small glass chip. Thin silicone rubber was used as a spacer. The thickness of the spacer was 100 μm . A set of rubber spacers, which were ca. 1mm in width and ca. 35 mm in length, were put on a cut slide glass (ca. $40 \times 26 \text{ mm}^2$). The distance between two spacers was set to be 5 mm. A cut cover glass was put on the

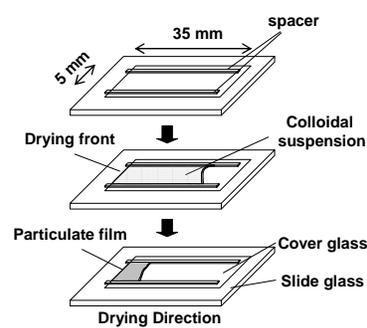


Figure 1. Handmade glass chip.

spacers in order to create a narrow space with two open ends. Because of good adhesion between the silicone rubber and glass surface, we do not have to use any glue to make glass chip.

Glass chip was put on a temperature control stage. After setting the glass chip, a slight amount of colloidal suspension was poured into the chip from one open end so that we can keep the air-liquid meniscus ca. 10 mm away from the other open side^[1]. Because the latter open side is filled with solvent vapor, evaporation of solvent mainly occurs from the open side filled with suspension, resulting in a unidirectional drying of colloidal suspension. A schematic illustration

is shown in Figure 1. We used an optical microscope (SMZ800, Nikon) for observation of suspension drying. Observed images were recorded by a digital camera (D1x, Nikon).

3. Results and Discussion

Typical examples of formed particulate films after complete evaporation of solvent water are shown in Figure 2. While many cracks along the drying direction with narrow spacing are formed, lateral cracks which are perpendicular to the drying direction also formed at a sample temperature of 50°C (Figure 2b). Spacing between each lateral crack increases from left to right. Drying temperature affects the lateral crack spacing. Drying of suspension at room temperature results in wider spacing (Figure 2b). Further decrease in drying temperature was carried out by putting the sample glass chip in a refrigerator (ca. 1°C). In this cold drying environment, we do not see any lateral crack formation (Figure 2c). This is one of the features in lateral crack formation. The spacing becomes wider when evaporation rate becomes slower. On the other hand, evaporation rate seemingly does not affect the spacing between cracks along the drying direction as shown in Figure 2. We consider that formation mechanism for lateral cracks is different from the one along drying direction.

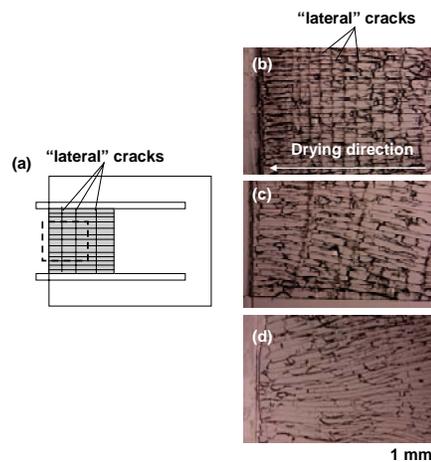


Figure 2 (a) Schematic image of a formed particulate film. The dashed square corresponds to the observed region shown in (b) to (d). Drying temperature was (b) 50°C, (c) room temperature and (d) 1°C, respectively.

Time evolution of both particulate film formation and crack formation is shown in Figure 3. We do not see any clear line right after injection of suspension (Figure 3b). However, we can see a black line on the right side of the crack front. This line corresponds to compaction front of dispersed particles. It is the boundary between dispersed-particles region (right side) and packed-particles region (left side)^[1]. As drying proceeds, dispersed particles flow to the evaporation edge. This flow is caused by strong capillary pressure which exerted on small meniscus between particles at the drying front. Then transported particles are packed at the compaction front. Further drying removes solvent from packed particles region, followed by the shrink of films and crack formation. The above description is a general physical picture for crack formation in

particulate film^[7]. Previous studies pointed out some relationship between crack formation and the compaction front. We are now studying lateral crack formation mechanism by monitoring the compaction front. In addition to it, we are also conducting quantitative analysis of evaporation effects on the lateral crack spacing. Detailed results and discussions are reported in our talk.

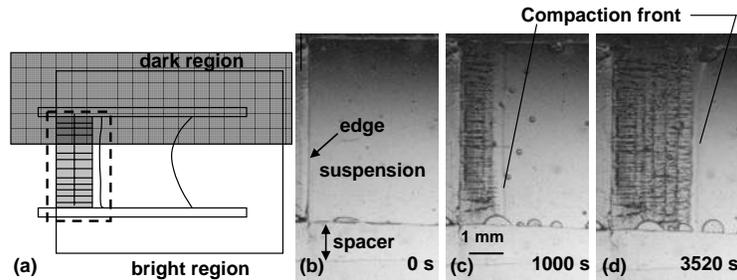


Figure 3. Time evolution of crack formation. (a) Schematic picture of an observed sample. The dashed square corresponds to observation area. Upper half of the chip was dark so as to clarify the compaction front of the particle film. Transmission images are shown in (b)-(d). These images were taken at (b) 0 s, (c) 1000 s and (d) 3520 s after injection of suspension, respectively. The sample temperature was 45°C.

4. Conclusion

We found that unique lateral crack formation during drying of colloidal suspension. Lateral crack formation shows different feature from the conventional cracking along the drying direction.

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