Transactions of the Materials Research Society of Japan 33[4] 1251-1254 (2008)

Blocking Characteristic of Aerosol Deposited Alumina on Plastics against Liquid

A. Iwata, J. Akedo and K. Handa*
National Institute of Advanced Industrial Science and Technology, 1-2-1 Namiki, Tsukuba-shi 305-8564
Fax: 81-29-861-7091, e-mail: iwata.a@aist.go.jp
*Mitsubishi Chemical Corporation, 14-1, Shiba 4-chome, Minato-ku, Tokyo 108-0014
Fax: 81-3-6414-3698, e-mail: 2400054@cc.m-kagaku.co.jp

Aerosol deposition, based on room temperature impact consolidation (RTIC), can form aluminum oxide films on some of the plastics. However the characteristics of these films are not yet known much. One of the important characteristics of ceramic films on plastics is to block liquid to protect the plastic substrates. This may also give information on the structures of aerosol deposited films on plastics. So blocking characteristic of aerosol deposited aluminum oxide films on polycarbonate plates was evaluated with liquid acetone. Polycarbonate becomes clouded when liquid acetone is poured on. Therefore the state of substrate polycarbonate can show whether the aluminum oxide films effectively blocked the liquid by pouring acetone on the films. The aerosol deposited thin aluminum oxide films could not block acetone, and the whole area covered by acetone becomes clouded. In thicker films the residual stress in the films cause many cracks initiated from attacked points by acetone and frequently aluminum oxide films were peeled off from polycarbonate substrates. When the thickness is over 10μm, the films could block acetone. This suggests the existence of minute pores in the aerosol deposited films on plastic substrates.
Key words: Aerosol deposition, Alumina films, Plastic substrates, Blocking liquid

1. INTRODUCTION

Aerosol deposition, based on room temperature impact consolidation (RTIC) is very promising for ceramic film forming. It can form ceramic films on glass, ceramics and metals and even on some of the plastics. For example aluminum oxide, Al_2O_3, could be deposited on Nylon 6 and polycarbonate, but could not be deposited on polytetrafluoroethylene (teflon) or acrylic. [1] The aluminum oxide films were crystalline and had alpha alumina structure, which was the same structure as the precursor powder of aerosol deposition. However the characteristics of these films on plastics are not yet known much.

One of the supposed important rolls of ceramic films on plastics is to block off liquid to protect the surfaces of substrate plastics. For this purpose, characteristics to stop liquids from penetrating the aerosol deposited ceramic films on plastics should be known. However no study was found. These liquid stopping characteristics of films may also give information on the structures of aerosol deposited ceramic films on plastics.

Therefore the blocking characteristic of aerosol deposited aluminum oxide films on polycarbonate plates were evaluated with liquid acetone. Polycarbonate surface becomes clouded when liquid acetone is poured on. If the aluminum oxide films cannot block off acetone, the state of substrate polycarbonate surfaces under the aluminum oxide films change when acetone is poured onto the films on polycarbonate substrates. If the aluminum oxide films effectively block off acetone, no change is observed in the substrate surfaces.

2. EXPERIMENTAL

Aerosol deposition experiment was carried out with a standard aerosol deposition machine developed by us.

The substrates were polycarbonate plates (Mitsubishi Plastics, Inc. Stella S300) of the size of 50 mm by 50 mm and thickness of 1 mm. The plates were cut out by a guillotine from a large plate.

The precursor powder used was aluminum oxide (Al_2O_3) with alpha alumina structure. (Showa Denko K.K. AL-160 SG-3) It has nominal median particle size of 0.59 μm.

The carrier gas was nitrogen. The flow rate of nitrogen was mainly 3 l/min. The vacuum pressure of the deposition chamber varies with the flow rate of the nitrogen, and was about 100 Pa during the deposition.

The nozzle had 10 mm by 0.4 mm opening. The aerosol was ejected upward from the still nozzle. The nozzle was inclined in the range of 0 to 30 degree. The definition of inclination is shown in Fig. 1. The length of aerosol beam between the nozzle exit and the substrate was set to 10 mm. The

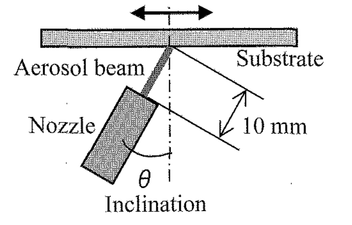


Fig. 1 Arrangement of nozzle and substrate

substrates were moving above the nozzle in a reciprocating motion. The length of the motion was 10 mm and the velocity was 15 mm/s. With the 10 mm nozzle opening and 10 mm displacement, the resulting size of the deposited films was around 10 mm by 10 mm.

The film thickness was measured with a diamond stylus profilometer. (Tokyo Seimitsu Surfcom 480A) The contour traces of the aluminum oxide films and surrounding substrates were measured. Normally the substrates and films were bent with convex film side. The bending amounts of the films were measured from the original trace curves as shown in Fig. 2. The original curves were then corrected with circular curves. From the corrected curves the film thicknesses were measured.

The acetone test was carried out under a stereo microscope. One milliliter of acetone was poured onto the aluminum oxide films repeatedly. If the films stop acetone from penetrating, acetone on the films soon disappeared and no changes were observed. If acetone penetrated the films, it attacked the polycarbonate substrates underneath and the poured area became white or cracks appeared in the films. If acetone flowed out of the films, cracks initiated from the edges of the films because the substrates surrounding the films were attacked and the stress balance at the edge was broken independent of acetone penetration of the films. Therefore small amount of acetone was repeatedly poured on not to cause unintentional flow of acetone on the films.

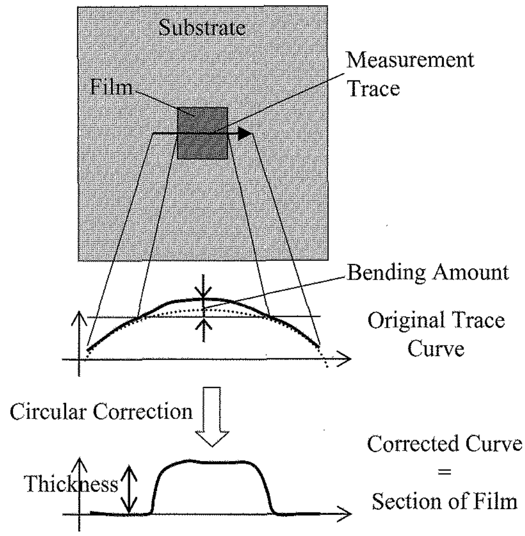
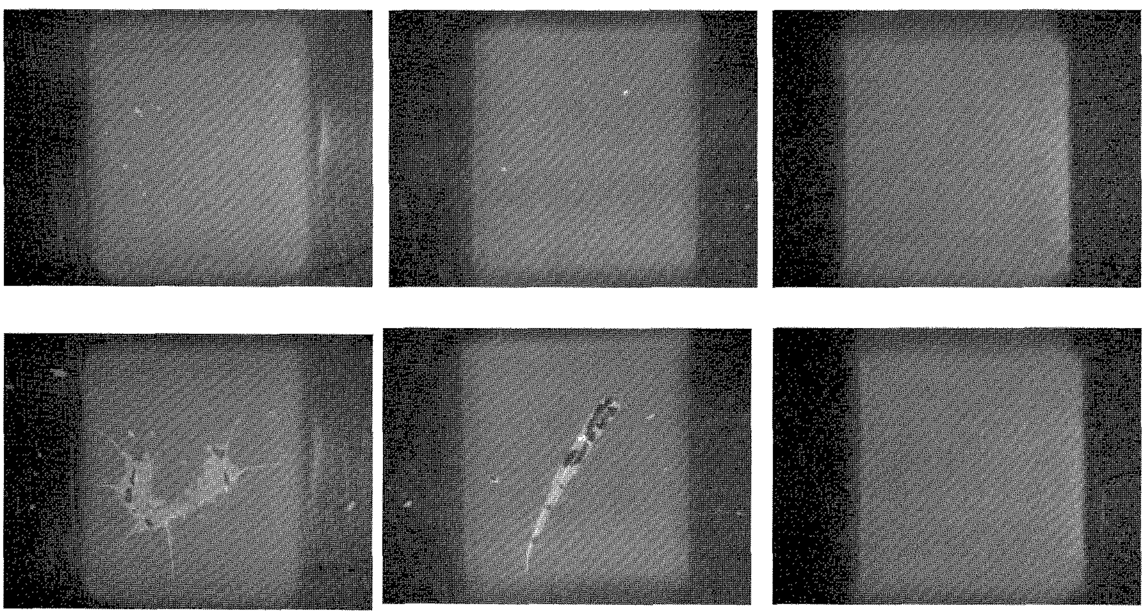


Fig. 2 Film thickness measurement by diamond stylus profilometer

3. RESULTS AND DISCUSSION

Aluminum oxide films deposited by aerosol deposition had surface defects when their thickness is large as shown in Fig. 3. The surface defects are seen as white dots in the upper pictures of Fig. 3, and are small dents in the films. However as the inclination angle of nozzles became larger, number of the surface defects became smaller. Major defects disappeared at the inclination angle of 30 degree.

In the acetone tests these surface defects frequently became the starting points of cracks induced by acetone as shown in the lower pictures of Fig. 3. The deposited films in the figure have the size of 10 mm by 10 mm. Two major surface defects are seen in the picture of 12.2 μm thick film. On pouring acetone, the one in upper



Thickness 11.7μm 12.2μm 14.5μm

Inclination θ 0 degree 20 deg 30 deg

Upper pictures: As-deposited aluminum oxide films, Lower pictures: Films after acetone test

Fig.3 Effects of nozzle inclination on surface defects right part became the starting point of the big crack shown in the films after acetone test picture. Another surface defect in left part did not initiate a crack, but became larger and seemed to have penetrated the film. The white dot in right part of the films after acetone test picture that did not appear in the upper picture is the peeled off fragment of the film from the big crack nearby. The white areas along the cracks are films peeled off from the substrates and yet stayed in the same place.

The process of aerosol deposition does not consist of deposition only. It is composed of deposition and abrasion by incoming particles. As the inclination angle becomes larger, abrasion becomes stronger and finally abrasion of the substrate takes place. [2] With the good balance of deposition and abrasion which was found at the inclination angle of 30 degree in this experiment, the film surface was deposited while planed by abrasion. Therefore the good surface without defects could be formed.

Without surface defects the 14.5 μm thick film did not show any change when acetone was poured on repeatedly. Namely thick aluminum oxide films could block off acetone effectively.

Fig. 4 shows the results of acetone test for films with various thicknesses. They are deposited with 30degree inclined nozzle.

When one drop of acetone was poured on the films, it spread out as a circle. When a drop was poured on the films less than 1 μm thick, all over the area where acetone covered turned to white. One example is the 0.3 μm thick film shown in Fig. 4 where white circle was seen.

In the case of thin films like the 2.0μm thick film in Fig. 4, the area acetone covered was filled with small cracks with various orientations. The cracks do not propagate much outside of the area where acetone covered.

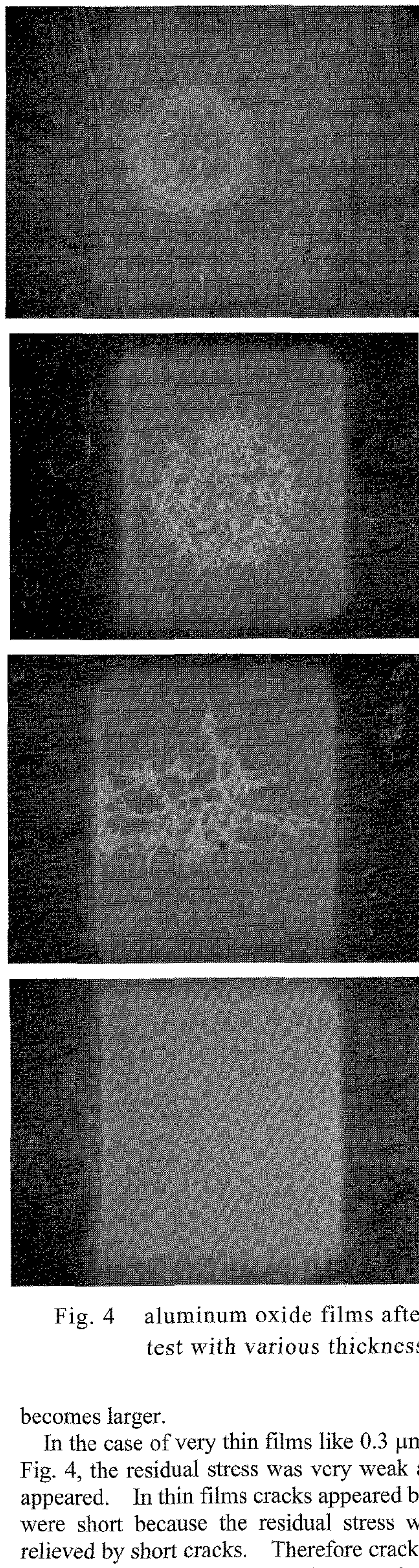
When the thickness of aluminum oxide films became larger, like the 9.1 μm thick film in Fig. 4, the cracks became longer and their numbers became smaller. Also the cracks did not fill fully the area where acetone covered, and propagated longer outside of the area. Consequently the cracks did not show where acetone was poured on. Additional drops of acetone made more cracks and more white peeled off areas.

Finally when the thickness of the films was over 10 μm, no change was observed in the films as shown in the 12.7 μm film in Fig. 4, even if pouring on of acetone was repeated many times.

From these experiments it can be said that aluminum oxide films that are about 10 μm and over thick can block off acetone as long as they have no surface defects.

These variations of surface after acetone test may be understood from the view points of residual stress in the films and minute pores in the films.

The deposited substrates are normally bent, and the deposited films are on the convex side. This suggests the existence of residual stress in the deposited films. Fig. 5 shows the amount of bending for various film thicknesses. The amount of bending can be seen as the index of magnitude of residual stress. From the figure the residual stress increases as the thickness of the films becomes larger.



Film thickness 0.3 μm

2.0 μm

9.1 μm

12.7 μm

Fig. 4 aluminum oxide films after acetone test with various thickness

In the case of very thin films like 0.3 μm thick film in Fig. 4, the residual stress was very weak and no cracks appeared. In thin films cracks appeared but their length were short because the residual stress was small and relieved by short cracks. Therefore cracks were mostly confined in the acetone poured area and did not spread out of the areas much. When the thickness became larger and the residual stress also became stronger, cracks tended to be longer. As seen in the 12.2 μm thick film in Fig. 3, cracks cover the full length to the edge of the film when the thickness was over 10 μm.

Therefore cracks were initiated in the acetone poured area, but ran independent of the area.

When the films were very thick, due to the strong residual stress, the films were sometimes almost completely destroyed on pouring acetone as shown in Fig. 6. Thick films can stop acetone. However, once something bad happens, thick films have the potential to be destroyed completely.

Fig. 7 shows the optical micrographs of the 0.3 μm thick film shown in Fig. 4. Many small white dots (less than 1 μm diameter) are seen in the picture of acetone poured area of the aluminum oxide films. These dots are not seen in the picture of the part of the film that was not poured acetone on. These white dots are the points that the substrate polycarbonate was attacked by acetone. The fact that these dots are independent each other means acetone independently penetrated the aluminum oxide films, and there are many small penetrating pores in the film of this thickness.

When the thickness is 0.3 μm the film had many pores that let acetone pass through. When the thickness was 2.0 μm, small white spots were not seen and the points that let acetone pass through were considered to be the initial points of cracks. The number of these points was much less than the white small points in 0.3 μm thick film. The number of these points decreased in 9.1 μm thick film, and these points disappeared in 12.7 μm thick film.

The nozzle scanned the full area of the film once in 0.67 s. These films were deposited in several minutes. So the film was made by several hundreds of scans. Namely the film consisted of many thin component layers that are not necessarily perfect layers. So the component thin layers had many pores that let acetone pass through. However each component layers has pores at different positions. Therefore piling up many component layers reduces the probability of penetrating pores. And about 10 μm thick film had almost no penetrating pores.

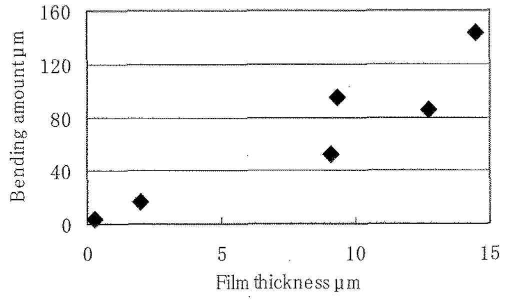


Fig. 5 Bending amount and thickness of the films

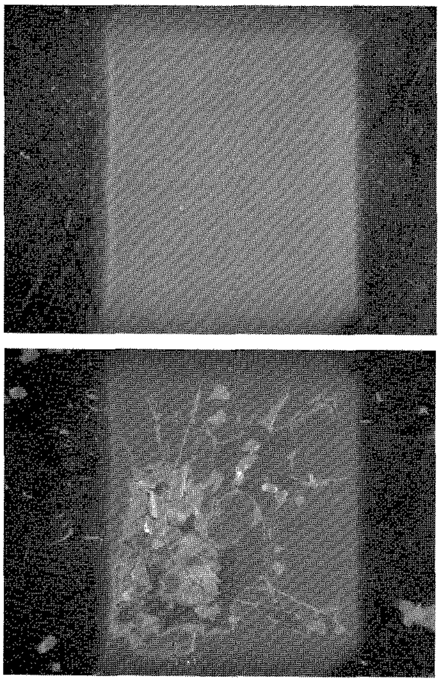


Fig. 6 Thick Film was almost completely destroyed by poured acetone. Upper picture is as-deposited film with a surface defect and had 9.3 μm thickness. Lower is the film after pouring acetone.

4. CONCLUSION

Acetone was poured on aluminum oxide films made by aerosol deposition on polycarbonate plate. Thin films could not stop acetone from penetrating the films. Many pores in the films were supposed. About 10 μm thick films could effectively block off acetone.

REFERENCES

[1] M. Mori and J. Akedo, *Proc. 21st Inter. KOREA-JAPAN Seminar Ceramics*, **21**, 49-52 (2004).

[2] M.Lebedev, J. Akedo, *Ferroelectrics.*, **270**, 117-122 (2002).

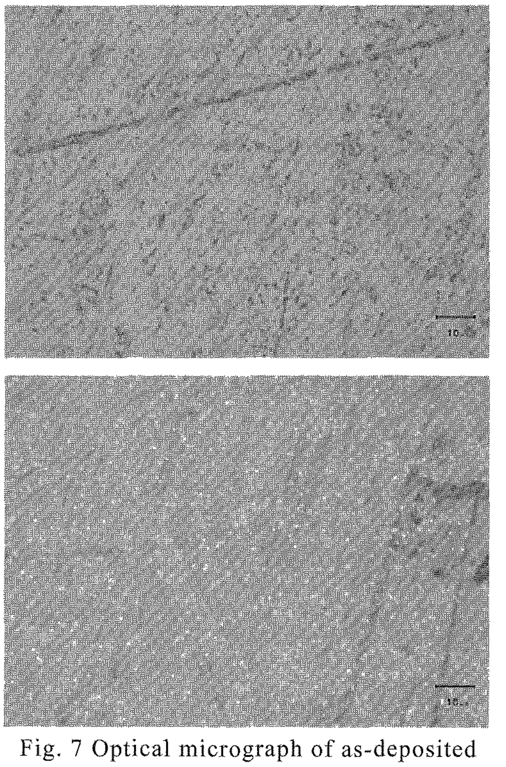


Fig. 7 Optical micrograph of as-deposited film (upper) and acetone poured film (lower)

(Recieved December 8, 2007 ; Accepted July 7, 2008)