

TIONS

THIS

MEN

RE

IBLE

CONF-81113--14

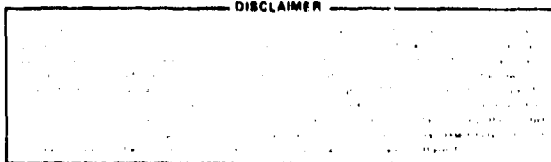
Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE: VACUUM DEPOSITION OF HIGH-QUALITY METAL FILMS ON POROUS SUBSTRATES

AUTHOR(S) Barry L. Barthell and David V. Duchane

SUBMITTED TO 28th National American Vacuum Society Symposium,
Anaheim, CA, November 1981

DISCLAIMER



[Handwritten signature]

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.



Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

VACUUM DEPOSITION OF HIGH QUALITY
METAL FILMS ON POROUS SUBSTRATES

Barry L. Barthell, David V. Duchane
Los Alamos National Laboratory

Abstract

A composite mandrel has been developed consisting of a core of low density polymethylpentene foam overcoated with a thin layer of film forming polymer. The surface tension and viscosity of the coating solution are important parameters in obtaining a polymer film which forms a continuous, smooth skin over the core without penetrating into the foam matrix. Water soluble film formers with surface tensions in the range of 45 dynes/cm and minimum viscosities of a few hundred centipoises have been found most satisfactory for coating polymethylpentene foam.

By means of this technique, continuous polymer films with thicknesses of 10-20 μm have been formed on the surface of machined polymethylpentene foam blanks. Aluminum has been vacuum deposited onto these composite mandrels to produce metal films which appear smooth and generally defect free even at 10,000 times magnification.

INTRODUCTION

The substrate plays a key role in the fabrication of thin metal films by vacuum deposition, since any defects or irregularities in the surface of the substrate tend to be reproduced in the film.¹ Further, if a freestanding film is to be produced, the substrate must be removed after deposition of the film material. This can readily be accomplished with parting agents when films are formed as flat sheets of moderate size, but when they are to be made with closed shapes such as cylinders or spheres, removal of the mandrel is much more difficult. In these cases mandrels are generally removed by leaching processes which may be very time consuming. Mechanical agitation is often employed in the leaching process, but this poses a risk to the integrity of the thin film. In addition, the leaching fluid itself must be carefully chosen. Metal mandrels require leachants which may be corrosive, difficult to handle, and prone to attack the thin film itself if parameters such as temperature and pH are not carefully controlled. Polymeric mandrel materials, while soluble in organic liquids which pose no danger to the deposited metal film, are usually slow to dissolve and often swell noticeably prior to becoming completely fluid. Such swelling can destroy the deposited shell.

The ultimate goal of the work reported herein is the development of a composite mandrel consisting of a core of low density, open cell, polymeric foam, overcoated with a thin

layer of a smooth polymer film. Such a mandrel would have a microscopically smooth surface, an extremely high surface to mass ratio, and an effective void volume approaching 95%. These qualities would largely obviate many of the problems associated with the fabrication of metal-walled fusion targets. The smooth surface would permit the deposition of metallic films of good strength and uniformity. Leaching would be facilitated by the high surface to mass ratio, or could possibly be eliminated entirely by simply filling the voids with fuel and leaving the foam core as a permanent structural support.

Coating of polymer foams has been practiced in the plastics industry for a number of years, but microscopically smooth finishes have not generally been among the goals of coating processes.² Such surface smoothness as has been achieved often involves the use of fillers and relatively thick coatings.^{2,3}

It has been the primary object of this work to develop coating materials which will form continuous thin films on the surface of a low density, open cell foam without penetrating significantly into the body of the foam structure. As will be shown below, the surface tension and viscosity of the coating solution are important factors in the success of this technique.

EXPERIMENTAL

The polymer foam used in this work was obtained by a process recently developed at the Los Alamos National Laboratory.⁴ It consists of polymethylpentene, and is originally produced as a filled material. For these experiments, the filled foam was first machined into hollow cylinders 23-mm long and 13 mm in diameter. The filler was then leached out to yield a mandrel core of low density (about 0.05 g/cm^3), open cell, pure hydrocarbon material. At this stage of the process, the surface of the foam was macroscopically smooth but microscopically rough and porous with an average cell size of about $25 \text{ }\mu\text{m}$.

In each trial the coating solution was applied to the surface of the foam by lowering the core into the coating liquid on a rod extended through its center until it was totally immersed, and then withdrawing it at a constant rate of about 15 mm/min . The excess coating fluid was allowed to drain from the surface while the sample was suspended vertically.

The samples were dried in a laminar air flow hood to minimize dust contamination. After drying, each sample was inspected visually and by scanning electron microscopy (SEM). Aluminum was vapor deposited onto samples of foam coated with the most promising formulations, and the aluminized surfaces again examined by SEM.

The coating solutions were prepared by dissolving polymers known to be good film formers in water or methanol. The materials and concentrations were chosen to give solutions with a wide range of surface tensions and viscosities. Each solution was colored red to make visual observation of its behavior during the coating process easier to observe. Tests showed that the dye (Eosin B at 0.1% concentration) did not affect the surface tension or viscosity of the solutions.

Surface tension measurements were made by the du Nouy ring method with a Fisher Model 20 Surface Tensiometer. Viscosities were determined with a Brookfield Model LVT Viscometer.

RESULTS AND DISCUSSIONS

The important properties of the film forming solutions used in this work are summarized in Table I. These solutions have surface tensions ranging from a high value only 8 dynes/cm below that of pure water down to values typical of many common organic solvents.⁵ The lowest viscosity material has a consistency similar to that of water while the highest viscosity solution is about as thick as table syrup. The numerical designations given in Table I will be used when referring to specific solutions in the discussion which follows.

Figure 1a shows polymethylpentene cylinders after coating with solution Nos. 1, 3, and 5. These have similar viscosities

but surface tensions of 68, 45, and 27 dynes/cm respectively. It is apparent that the high surface tension solution did not thoroughly wet the surface of the foam. As a result only blotches of film were formed on the surface of the cylinder. The liquid of intermediate surface tension formed a smooth coating on the surface of the foam but did not appear to penetrate into the body of the cylinder. As indicated by the depth and uniformity of the color of the third cylinder, the low surface tension solution soaked into the pores of the foam, and in effect, filled it. Since all the coating solutions were of about the same color intensity, the differences in color of the coated cylinders provide a good qualitative guide to the behavior of the coating solutions.

Figures 1b-d show SEM's of the surfaces of the three cylinders pictured in Fig. 1a. This microscopic view reveals that even the portion of the cylinder treated with solution No. 1 (Fig. 1b) which did accept a coating had a surface marked by swirls and craters. The surface of the foam coated with solution No. 3 (Fig. 1c), while not absolutely smooth, shows only minor surface irregularities. Rather than being pits or pointed projections, these irregularities are in the form of troughs or mounds with gently sloping walls. It is known that a high angle of incidence may be important to obtaining high strength metal films by vapor deposition.⁶ Gentle undulations do not pose the problem that pits and points do in this regard.

The surface coated with solution No. 5 (Fig. 1d) is seen to be cellular in nature, indicating no significant bridging of the pores of the polymethylpentene foam.

The importance of surface tension in this coating process is further illustrated in Fig. 2. Here SEM's of the surfaces of foam cylinders coated with solutions No. 4 (Fig. 2a) and No. 6 (Fig. 2b) are shown. Both surfaces were coated with the same type of polymer (although the molecular weight of the polymer was somewhat higher for solution No. 6), but from different solvents. Again, the solution having a surface tension of intermediate value is seen to produce a relatively smooth surface, while the low surface tension liquid, even though higher in viscosity, does not adequately bridge the pores in the foam.

The quality of the surface coating on the polymethylpentene foam is also somewhat dependent upon the viscosity of the coating solution. This is shown in Fig. 3 which is an SEM of the surface of a foam cylinder coated with solution No. 2. While this was the same polymer used to coat the foam shown in Fig. 1b, and the superficial appearance of the cylinder after coating was similar, the lower viscosity of this solution led to excessive runoff and incomplete bridging of some of the foam pores. The fact that a majority of the cells were closed by this coating indicates that the concentration of the polymer was high enough to permit film formation to take place.

The thicknesses of the two polymer films which produced continuous, smooth surfaces on the polymethylpentene foam (solutions No. 3 and 4) can be estimated from SEM's of cross sections of foam cylinders coated with these solutions. These SEM's are shown in Fig. 4. In both cases, the outer continuous layer appears to be on the order of 10-20- μm thick. The SEM's also indicate that these polymer coatings are confined essentially to the surfaces of the foam cylinders.

Finally, Fig. 5 shows an SEM of the surface of a 5- μm -thick aluminum/aluminum oxide film vacuum deposited onto a polymer coated polymethylpentene foam sample using the pulsed gas process.⁷ In this case, the polymer coating was applied by dipping in solution No. 2, but the sample was a flat disk rather than a cylinder. This SEM illustrates the extremely smooth aluminum films which may be obtained by this technique.

CONCLUSIONS

A composite mandrel composed of a core of polymer foam overcoated with a thin, smooth, polymer film can be used as a substrate for the vacuum deposition of high quality metal films. The surface tension and viscosity of the coating solution are key properties in the fabrication of such a composite mandrel. For hydrocarbon foams such as polymethylpentene, the coating solution should have a surface tension in the range of 45 dynes/cm, and certainly greater than 30 dynes/cm. Since many common organic liquids have surface tensions lower than

this value,⁵ water-based film forming solutions would seem to be particularly suited for coating hydrocarbon foams.

The viscosity of the coating solution must be above a certain minimum to ensure adequate bridging of the foam pores. For polymethylpentene with an average cell size of 25 μm this minimum has been found to be a few hundred centipoises. Higher viscosities might be expected to lead to thicker polymer coatings. At extremely high viscosities it is likely that the material would stiffen before leveling took place and the desired smooth surface would not be realized.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Ainslie T. Young for supplying and leaching the polymethylpentene foam used in this work and David Murphy for machining this unique material to close tolerances. The work of Chuck Javorsky in preparing the SEM's used in this paper is also gratefully acknowledged.

REFERENCES

1. L. Maissel and R. Glang, Editors, Handbook of Thin Film Technology (McGraw-Hill, New York, 1970)
2. C. D. Storm, *Plastics Engineering*, 36, (8), 36 (1980).
3. Anonymous, *Plastics Technology* 24, (12), 117 (1978).
4. A. T. Young, D. K. Moreno, and R. G. Marsters, Paper No. VFWM-15, American Vacuum Society, 28th National Symposium (1981).
5. R. C. Weast, Ed., *Handbook of Chemistry and Physics*, 52nd Edition (Chemical Rubber Co., Cleveland, Ohio, 1971).
6. R. W. Springer and D. S. Catlett, *Technical Digest of Conference on Inertial Confinement Fusion* (1980).
7. R. W. Springer and D. S. Catlett, *Thin Solid Films*, 54, 197 (1978).

FIGURE CAPTIONS

Fig. 1 a. Photograph of foam cylinders coated with high, medium, and low (l to r) surface tension film formers. b-d. SEM's of the surfaces of these cylinders. Note the superiority of the surface coated with the medium surface tension film former.

Fig. 2 SEM's of surfaces of foam cylinders coated with hydroxypropylcellulose (HPC) from intermediate and low surface tension solutions.

Fig. 3 SEM of surface of foam coated with low viscosity polyvinyl alcohol solution.

Fig. 4 SEM's of cross sections of foam cylinders coated with good film formers. Note the continuous film at the surface of each cylinder.

Fig. 5 SEM of Al/Al₂O₃ laminate vacuum deposited of foam/film composite mandrel.

TABLE I. Important Properties of Film Forming Solutions

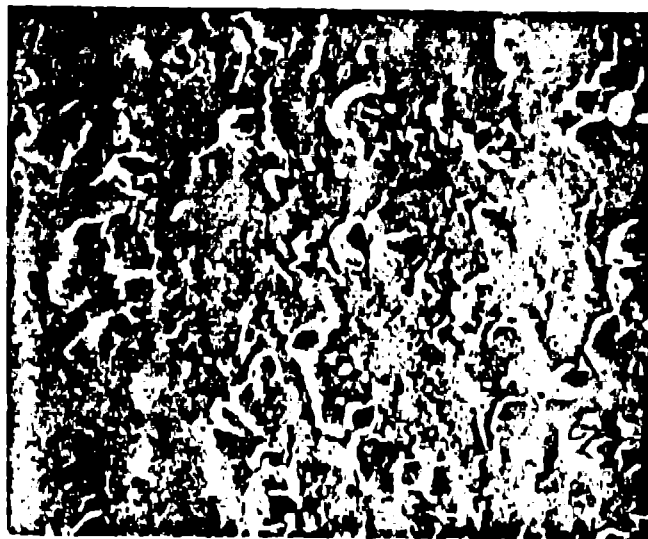
<u>Solution No.</u>	<u>Film Forming Polymer</u>	<u>Solvent</u>	<u>Polymer Concentration (%)</u>	<u>Surface Tention(dynes/cm)</u>	<u>Viscosity (cps)</u>
1	CMC-7L ^(a)	Water	5	68	180
2	Polyvinyl Alcohol, 88% hydrolyzed	Water	10	45	30
3	Polyvinyl Alcohol, 88% hydrolyzed	Water	20	45	480
4	Klucel E ^(b)	Water	15	45	1300
5	Klucel E ^(b)	Methanol	15	27	270
6	Klucel J ^(b)	Methanol	15	28	3000

^a CMC is a trademark of Hercules Inc. for Sodium Carboxymethylcellulose.

^b Klucel is a trademark of Hercules Inc. for Hydroxypropylcellulose.



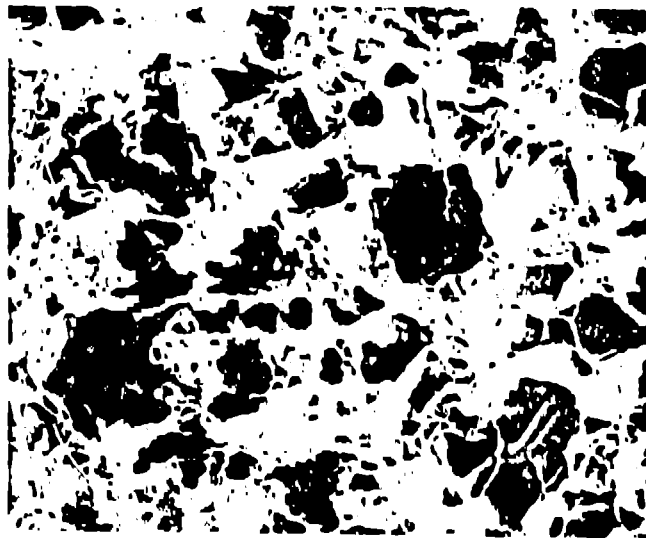
a



b

50 μm

68 dynes/cm



d

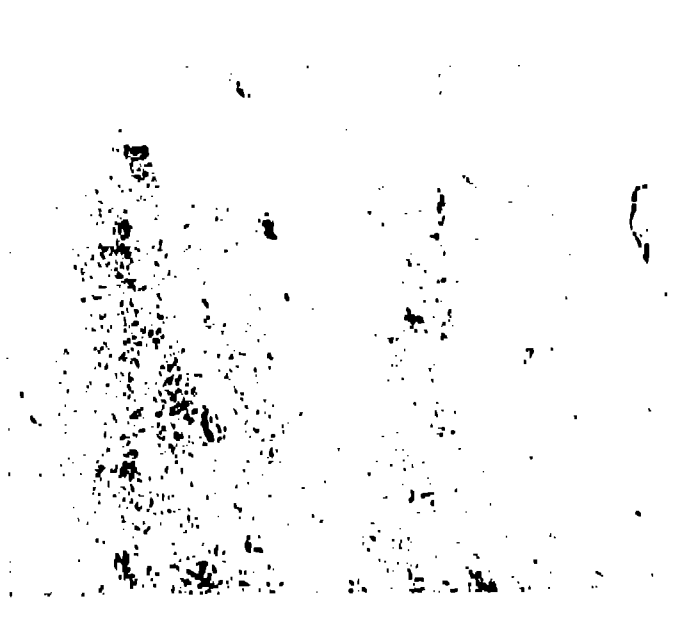
50 μm

27 dynes/cm

45 dynes/cm

100 μm

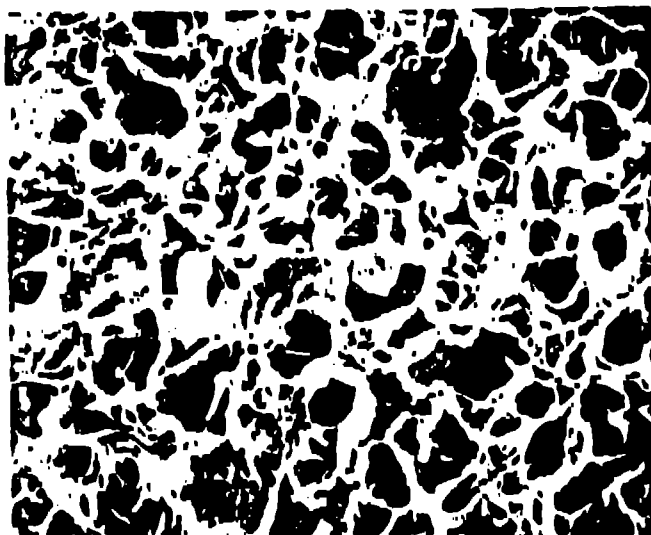
c



a

100 μm

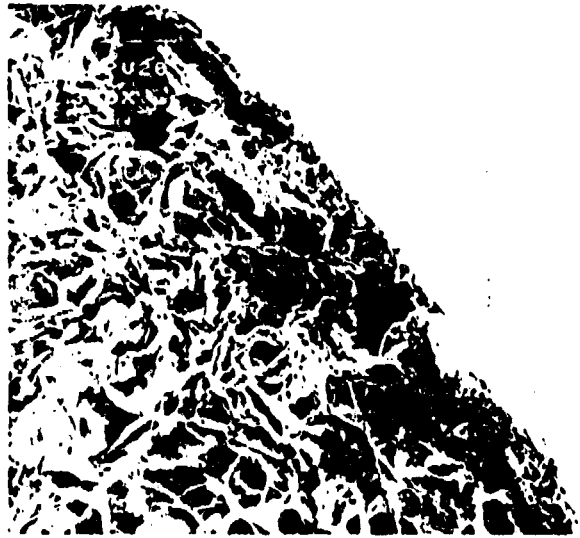
45 dynes/cm



b

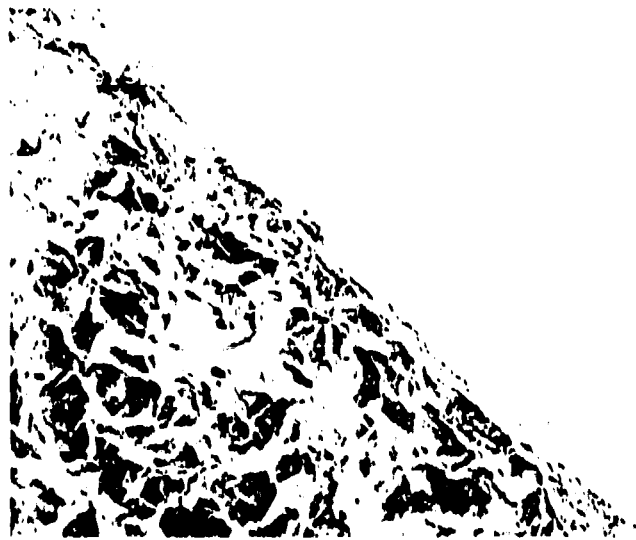
50 μm

28 dynes/cm



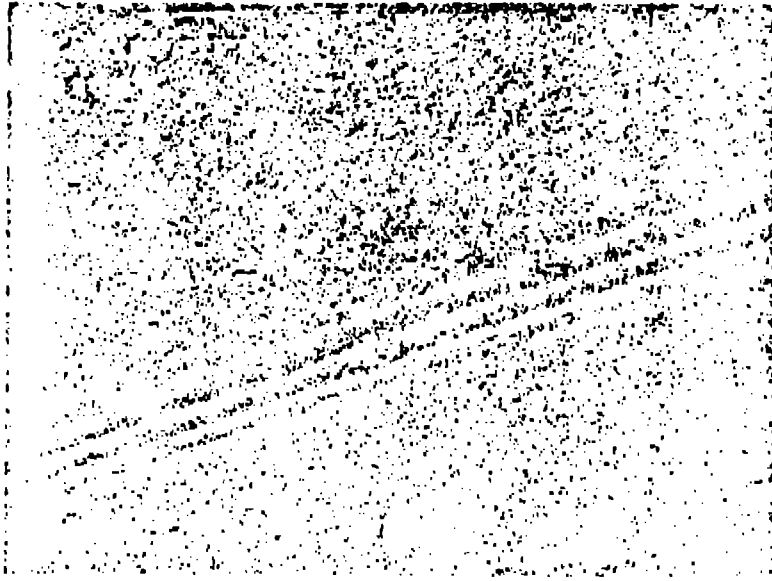
a

50 μm



b

50 μm



I
1 μm