Sonochemical Surface Modification of Expanded Polytetrafluoroethylene and Ferrite Plating
Masanori ABE, Minjuan ZHANG, Makoto OJIMA, and Yoshitaka KITAMOTO
Department of Physical Electronics, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract—By exposing expanded polytetrafluoroethylene (ePTFE) sheets to power ultrasound waves (600W, 19.5kHz) in an aqueous solution of B(OH)₃, the wettability of the surface was increased. The radicals H*, B*, OH* generated in "hot spots" (caused by collapse of cavitation bubbles) cut C-F bonds and generate C-OH bonds on the surface, which increase the wettability. On the sonicated surface of the ePTFE sheets uniform Fe₃O₄ layers were successfully grown from an aqueous solution of FeCl₂ by ferrite plating.

I. INTRODUCTION

Expanded polytetrafluoroethylene (ePTFE, PTFE is trade-named as teflon) has been put to such practical medical uses as unwoven sheets for surgical patches [1] and tubes for artificial vessels [2]. Being a fluoropolymer having no indigenous reactive functional groups (e.g. hydroxyl, amino, etc.), PTFE exhibits on its surface low wettability and poor biocompatibility as well as weak joint strength with commonly encountered adhesives. To improve these property, the following surface modifications, which introduce the lacking functional groups, have been devised: (a) chemical treatments [3], (b) vapor deposition of Al followed by aqueous removal [4], (c) plasma treatment in vacuum [5], and (d) ultraviolet light treatment in a H₃BO₃ aqueous solution or in an NH₃ gas [6].

These methods have inevitable shortcomings, however: (a) must use hazardous chemicals; (b) and (c) use vacuum, which is complicated in handling; and (b), (c), and (d) cannot uniformly improve surfaces of complex shape due to shadow effects inherent in the plasma treatment, vapor deposition, and UV light exposure.

In this paper we report that exposing ePTFE patches to ultrasound waves in a H₃BO₃ aqueous solution enhances hydrophilicity or wettability of the surface. This method is free from the use of the hazardous chemicals, is relatively simple to perform, and does not suffer from the shadow effect.

We also report that the sonicated ePTFE patches were successfully coated with a magnetite (Fe₃O₄) layer by ferrite plating, a chemical method synthesizing ferrite films from an aqueous solution [7]. The Fe₃O₄ coating is expected to increase the biocompatibility, because leakage flux from Fe₃O₄ accelerates the proliferation of endothelial cells on the coating [8].
Fig. 2. Micrographs for water drops on surfaces of ePTFE sheet, unsonicated (a) and sonicated (b).

Fig. 3. SEM observation on ePTFE sheets, unsonicated (a) and sonicated (b).

Fig. 4. Change made by sonication in XPS spectra of O(1s) and C (1s) lines obtained for ePTFE sheets.

Fig. 5. SEM observation on magnetite layer sonicated in H₃BO₃ aqueous solution.
Sonication increased the intensity of the spectral lines corresponding to the C-OH and C-O bonds, while the line intensity corresponding to C-F bond decreased.

On the sonicated and unsonicated ePTFE sheets we performed spin spray ferrite plating [7] at 80°C for 30 min, using a reaction solution (pH=5.2) of FeCl₂ and an oxidizing solution (pH=6.8) of NaNO₂ + CH₃COONH₄ (a pH buffer). The sonicated surface was coated by a uniform layer of single phase magnetite (Fe₃O₄), as revealed by X-ray diffraction, while no deposit was obtained on the unsonicated surface. The SEM photographs in Fig.5 shows that the magnetite layer was composed of grains angular in shape and ~1μm in size.

III. DISCUSSION: MECHANISM OF SURFACE MODIFICATION BY SONICATION

Since the sonication did not change the surface morphology (cf. Fig 3), the marked increase in the wettability is not ascribed to geometrical modification of surface texture but to the OH groups generated on the surface by dissociating the F bonded on C in PTFE. The power ultrasound waves produce in aqueous solution "hot spots" of extremely high temperature (~ 5000°C) and high pressure (~ 500 atm) due to adiabatic collapse of cavitation bubbles [9]. In the hot spots H₂O is dissociated into two radicals OH* and H*. Also B(OH)₃ is dissociated into radicals OH* and B*, as in the decomposition by excimer laser beams [10]. Then, as shown in Fig.6, the radicals H* and B* cut the C-F bonds, and the dangling C bonds thus made are terminated by the OH*, resulting in C-OH bond formation.

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\[ \text{H}^*, \text{B}^* \]
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\[ \begin{array}{cccc}
F & F & F & F \\
\cdots & C & C & C \\
F & F & F & F \\
\end{array} \rightarrow \begin{array}{cccc}
F & F & F & F \\
\cdots & C & C & C \\
F & F & F & F \\
\end{array} + \text{HF, BF} \]
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\[ \text{OH}^* \]
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\[ \begin{array}{cccc}
F & F & F & F \\
\cdots & C & C & C \\
F & F & F & F \\
\end{array} \rightarrow \begin{array}{cccc}
\cdots & C & C & C \\
F & F & F & F \\
\end{array} \]
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IV. CONCLUSION

The power ultrasound waves applied to ePTFE sheets in a B(OH)₃ aqueous solution increased wettability (hydrophilicity) of the surface, on which a uniform Fe₃O₄ layer was successfully deposited by ferrite plating.

The wettability increased because OH groups were generated on the surface by means of destruction of the C-F bonds of ePTFE by the radicals B*, H*, and OH* (which are created in the hot spots caused in the sonicated aqueous solution).

ACKNOWLEDGEMENT

This study has been financially supported by the "Research for the Future" Program, from the Japan Society for the Promotion of Science.

REFERENCES