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Note

Self-similar etching

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Abstract

When a fiber is brought into contact with a soft etching liquid, a conical tip is generally shaped. We show here that the use of corrosive liquids which release gases during the etching reaction may lead to original self-similar shapes, because of successive pinning and detachment of the meniscus. The conditions for the formation of this shape and its evolution are described. In particular, we stress the effect of convection due to released bubbles.

Keywords: Fibers; Etching; Wetting; Tip

1. Introduction

Chemical etching of fibers is a common technique for achieving conical tips [1–5], which can then be used as AFM tips or as connectors for optical fibers. The technique consists in immersing the fiber partially in a corrosive liquid. The liquid generally wets the solid surface, so that a meniscus rises along the fiber. If the fiber radius R is large, the balance between surface forces and gravity dictates the height of the meniscus to be of the order of the capillary length $\kappa^{-1} = (\gamma/\rho g)^{1/2}$, denoting as γ and ρ the liquid surface tension and density. For thin fibers ($R < \kappa^{-1}$), the axial curvature of the liquid/vapor interface due to the fiber geometry opposes the rise, and thus limits the meniscus height, which is found to be roughly proportional to the fiber radius [6,7]. More precisely, the profile of the meniscus is close to a catenoid, and its lateral extension fixed by the capillary length (above which the perturbation of the liquid/vapor interface due to the presence of a solid becomes negligible). The meniscus height can finally be written in the form $h = Rf(\kappa^{-1}/R)$, and James in [6] proposed an analytical approximation for the function f:

$$h \approx R\left[\ln(4\kappa^{-1}/R) - 0.577\right]. \tag{1}$$

This equation is in good agreement with the results obtained by Huh and Scriven, who integrated the Laplace equation numerically [7].

The height of the meniscus thus increases monotonically with the fiber radius. Since the etching reaction reduces this radius (in the immersed part of the fiber), we expect that the meniscus continuously moves down as the solid vanishes, if the observed shape results from successive quasi-static states. Such a process eventually leads to a tip whose profile is given by Eq. (1). For glass fibers etched at an interface between a HF solution and cyclohexane [1], Takahashi indeed found that the tip shape was very well described by this equation. In this note, we report that other choices of the couple fiber/acid may lead to very different tip shapes, which is shown to be due to the bubbling possibly associated to the chemical reaction.

2. Bubbly etching

2.1. Cuspidal tips

If a vertical copper wire of 1 mm of diameter (regular heavy duty electrical wire) is partially dipped into a concentrated nitric acid solution (50 vol%), intense bubbling results from the reaction at the liquid–solid interface: nitrogen oxide bubbles are released and burst at the liquid surface. Simultaneously copper ions are convected inside the acid reservoir,

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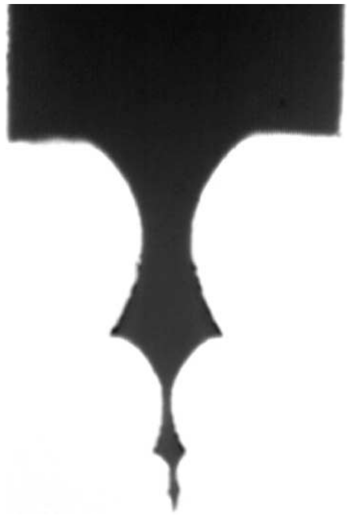

Fig. 1. Photograph of a tip obtained after placing a copper wire at the interface between a reservoir of concentrated nitric acid (50 vol%) (denser phase) and cyclohexane (upper phase). A cuspidal tip is etched at the place where the meniscus was standing. Similar shapes are obtained with air as the upper phase. Wire diameter: 1 mm.

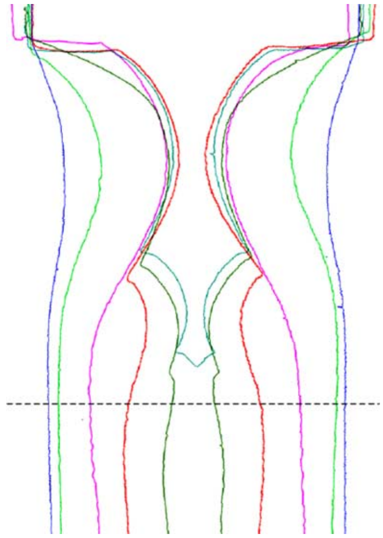

Fig. 2. Evolution of the wire profile during its etching by the acid solution (same system as in Fig. 1). The wire is pulled out of the bath after a time τ and photographed, from which the corresponding profiles can be extracted. They are drawn in blue ($\tau = 2$ min), light green ($\tau = 5$ min), pink ($\tau = 10$ min), red ($\tau = 15$ min), green ($\tau = 20$ min), and light blue ($\tau = 25$ min). The dashed line indicates the position of the surface of the liquid bath.

and the solution progressively turns blue. The reaction ends after about 20 min when the immersed solid has been etched. At the bottom of the remaining wire, a tip is produced, and its shape can be observed in Fig. 1. The profile is not regular, as in the usual situation but exhibits successive cusps and a self-similar pattern (with an aspect ratio base/height of 0.8 ± 0.1 for each of the four substructures).

Close-up imaging of the meniscus region during the etching process (achieved with a video camera equipped with a macro objective) indicates that the meniscus does not progressively move down. Instead, it remains pinned in a fixed position (corresponding to a cusp in the final shape) before it spontaneously jumps to the next one. Four of these successive detachments have been observed during the experiment reported in Fig. 1.

The evolution of the profile of the tip can be followed as a function of time by pulling the fiber out of the acid reservoir at different times (2, 5, 10, 15, 20, and 25 min) before its complete etching. The successive profiles of the "frozen" wires can then be extracted, as displayed in Fig. 2.

In a first step, a slight neck appears just under the meniscus, which indicates that the etching reaction is particularly efficient in this region. The difference with a classical etching (without bubbles) lies in the continuous supply of fresh acid, thanks to the liquid convection associated to the bubble motion. This leads to the production of overhangs, along which the contact line eventually slips, till it reaches a new equilibrium profile (solution of Eq. (1)). Then, the same mechanism applies, leading to a secondary structure at a smaller scale.

Note that during each step, the meniscus remains pinned at a fixed position (as we could observe thanks a movie of the process), which is made possible by the presence of edges on which the meniscus can pin [8]. In addition, it is observed that the motion of the bubbles does not affect the general shape of the meniscus, which keeps its static profile.

2.2. Bubbling and convection

As stressed above, cuspidal shapes are conditioned by the formation of necks, which provide lower equilibrium positions for the meniscus. The efficiency of the etching at the top of the meniscus (which is responsible for the achievement of a neck) was interpreted as an effect of the convection induced by the eruption of bubbles: fresh acid is driven to this warm region (the reaction is highly exothermic), while the etching products are quickly eliminated. Note also that because of the wetting of the wire by the acid, a continuous film of gas (which would stop the reaction) does not form along the fiber; instead, isolated bubbles grow and detach from the solid/liquid interface.

Bubbling can be reduced, either by the use of a dilute acid solution (of 25 vol%, for instance) or by gently bringing the fiber in contact with the liquid (instead of immersing it); in both cases, a conical tip is obtained. The fiber diameter must also be large enough (above 0.5 mm for the studied system): for a thinner wire, the neck shrinks and breaks above the level of the reservoir. The latter property can be used for designing tips with a large cone angle.

We can finally invert the convective flow: dense carbon tetrachloride (CCl_4) and lighter concentrated nitric acid are successively poured in a beaker and a copper wire (same diameter as above) is placed at the interface, as shown in Fig. 3a. The upper part of the wire is protected by a Teflon tape to prevent any etching in this region. The acid solution

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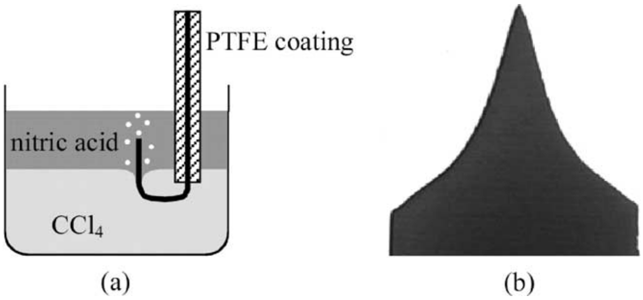

Fig. 3. Experimental setup providing inverted convection (a): a dense oil (here CCl_4) is poured into a beaker, and the wire (of diameter 1 mm) is placed at the interface between this oil and nitric acid. Since it is wet by the acid, the meniscus points downward. Note that in this configuration, the bubbles do not bring any fresh acid into the meniscus region. The resulting tip points upward and is found to be a regular one (b).

wets the wire, so that the meniscus at the interface between the two liquids is directed downward (Fig. 3a).

In this device, the bubble flow is therefore inverted, relative to the direction of the growing tip, if compared with the previous experiments. It cannot bring any fresh acid in the region where the meniscus thins, slowing down the reaction at this place. As a consequence, the meniscus should evolve by quasi-static steps, and a monotonic tip be achieved, as can indeed be observed in Fig. 3b.

3. Conclusion

Original cuspidal tips can be realized when a fiber is dipped in an etching liquid producing bubbles during the reaction. A strong bubbling provides a very efficient reaction in the upper region of the meniscus, which induces the formation of an angle on which the contact line can pin, and of a neck below. The meniscus eventually jumps to a second equilibrium region and successive similar steps finally lead to a self-similar shape. This qualitative description is in good agreement with the observations; for example, inverting the configuration restores the classical conical shape. Numerical calculations of the interfaces shapes combined with the simulation of the etching process would remain to be done, in order to capture quantitatively the effects of the different parameters (fiber diameter, etching rate, bubble radii, and velocity).

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