

Mercury spreading on silver films: interface characteristics

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ABSTRACT

We have studied the spreading of a liquid Hg drop on a Ag film. Geometrical characteristics of the propagating Hg spot front, its roughness and hull exponents have been investigated. The mechanism of Hg spot front formation has been analysed by optical microscopy, transmission electron microscopy, scanning electron microscopy and X-ray diffraction. We found that at short scales (up to about 20 μm) the roughness exponent of the Hg steady state interface is $\alpha \approx 1$ which is characteristic for self-similar objects. We also studied the hull exponent ν at these scales and found that $\nu = 1.3\text{--}1.7$. We suggest that on these scales a self-similar interface is generated by the process of invasion percolation. The invasion of Hg through the grain boundaries, which is observed at a high magnification, might be the origin of the roughening of the front interface. On larger scales the roughness saturates and the corresponding exponents are $\alpha = 0$ and $\nu = 1$.

§1. INTRODUCTION

The spreading and wetting of solid by liquid are complex physical chemistry and statistical physics phenomena. A modern view on this process has been reviewed by deGennes (1985). Dynamic interface roughening has been the subject of many recent studies, and the focus of many controversies in the last decade (deGennes 1985, Family and Vicsek 1985, Bunde and Havlin 1996, Barabasi and Stanley 1995).

The invasion percolation process has been described and applied to several recent interface formation experiments (Thompson *et al.* 1987, Rubio *et al.* 1989, Bunde and Havlin 1996, Buldyrev *et al.* 1992, Frette *et al.* 1997).

The roughness and hull exponents for the propagating front can be defined as in Bunde and Havlin (1996). The roughness $w(l)$ is a measure of the fluctuation of the front interface around its average position in the window size l . The interface is usually a self-similar or self-affine object. A self-similar object is an isotropic object with a fractal dimensionality d_f representing the scaling of mass with the size of the object L ($M = L^{d_f}$). A self-affine object is an anisotropic object and has different scalings in perpendicular directions. That is, if we change the scale $x \rightarrow ax$, then the change in scale of y is $y \rightarrow b^\alpha y$. The roughness exponent α characterizes the scaling of the width y as a function of the topological length scale x . If the interface structure resembles a straight line, its roughness exponent is smaller than unity. The hull exponent ν characterizes the scaling of the length of the part of the interface between two points with the physical distance between them. The hull exponent is unity for elongated interfaces and greater than unity for self-similar interfaces. For example,

the hull exponent is known to be 1.33 or 1.75 (depending on the exact definition) for the percolation clusters (Grossman and Aharony 1986).

The wetting and spreading of a liquid Hg drop on various solid bulk metal surfaces has been studied (Summ *et al.* 1987). The front propagation velocity has been studied as a function of time, the drop mass, and several hydrodynamic and physical-chemical models have been proposed to explain these results (Summ *et al.* 1987). However, to the best of our knowledge the spreading of Hg on *thin* metal films, its mechanism and the roughness of the spot interface front have not been explored. The study of the geometrical characteristics of the Hg propagation front may give information about the spreading mechanisms. The spreading on thin films is more complicated and several additional processes influence the pattern formation. For example, since the film is thin, we can observe the de-wetting phenomena of Hg on glass substrate. Usually all Ag from the film goes to the intermetallic compound and forms the net on the substrate. Also we can investigate in more detail the microstructure and grain boundary geometry since in an almost two-dimensional system they influence the front propagation more strongly.

In this paper we present experiments of Hg drop spreading on the surface of a Ag film deposited on a glass or Si substrate. This spreading is caused by wetting of Ag film by liquid Hg and the chemical reaction of Hg with Ag. We studied the geometry of the Hg propagation front interface and the mechanisms involved in the front formation. In particular, we studied the roughness and hull exponents of the spreading front interface, and these results suggest an invasion percolation process.

§2. SET-UP AND PROCEDURES

The Ag metallic films (20–120 nm thick) were deposited on glass microscope slides or Si wafers by evaporation. Drops of Hg of 10–50 μm diameter were placed on a clean metal film surface just after deposition. The spreading of Hg on the Ag surface was observed by an optical microscope equipped with the differential interference contrast accessories for contrast enhancement. The Hg front propagation was recorded with a video camera, which followed the Hg spreading front. The microstructure and phase composition in the vicinity of the interface were analysed by transmission electron microscopy (TEM), the spatial distribution of elements was determined by scanning electron microscopy (SEM) and the phase composition of thick films was determined by X-ray diffraction (XRD).

For the TEM observation the glass slides were first covered by photoresist (material soluble in acetone) above which a film of Ag 40 nm thick was deposited. Then a small ($d \approx 10 \mu\text{m}$) drop of Hg was placed on the film. The metal films with the reaction zone were lifted off using acetone and placed on a microscope grid for TEM observation. The optical microscopy images and the TEM images were analysed by computer programs in order to determine the geometrical properties such as roughness and hull exponents.

§3. EXPERIMENTAL RESULTS

Our experiments on the spreading of fluid Hg on Ag film display a rich behaviour, depending on the mass of the drop, the thickness of the Ag film, and the velocity of the spreading. This is because different mechanisms of Hg spreading play roles in the process. For example, wetting of the surface is faster at the beginning, invasion between grains is faster when the wetting velocity is small, and diffusion is

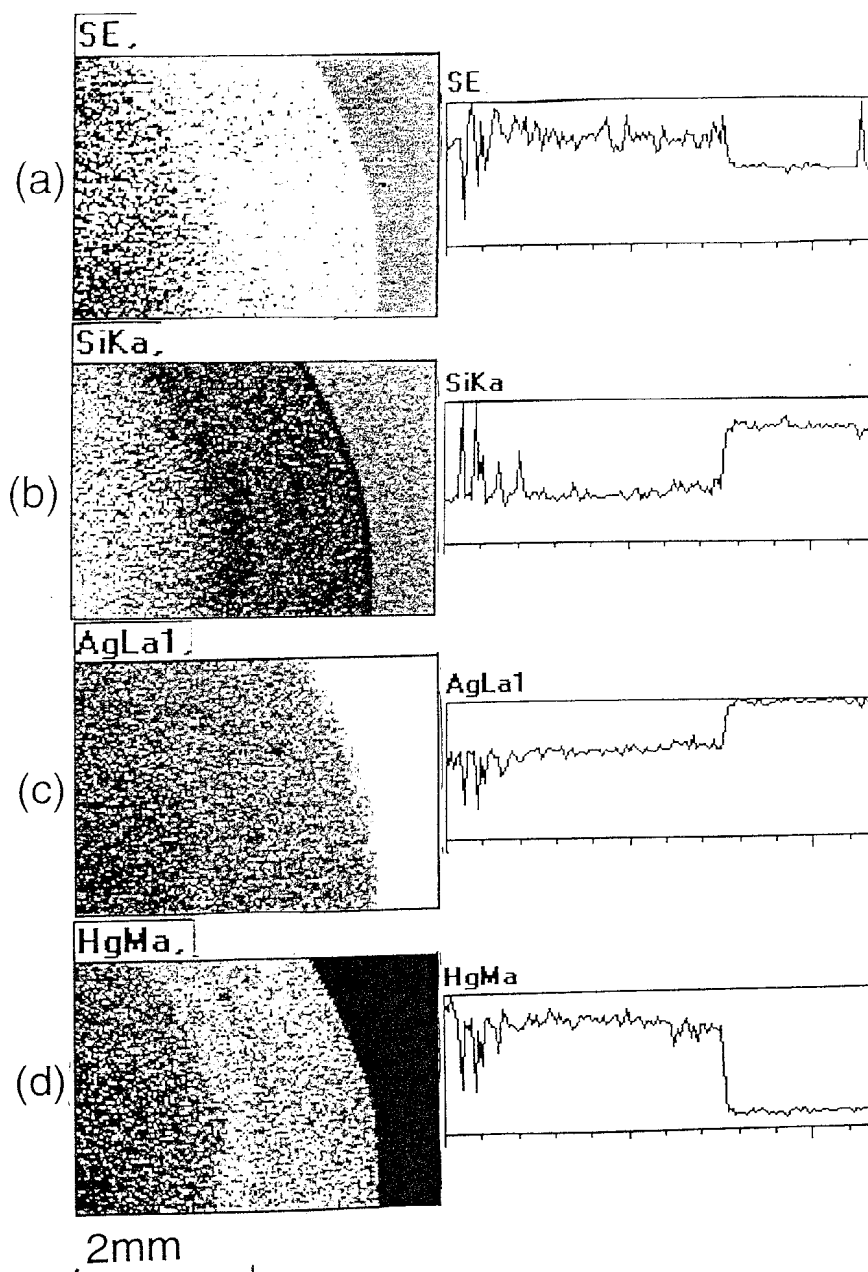


Figure 1. SEM images of Hg spreading on Ag film: (a) secondary electrons; (b)–(d) characteristic irradiation of (b) Si, (c) Ag and (d) Hg. The corresponding concentration profiles along a radius of the spreading spot are shown to the right.

faster when the liquid front propagation has almost stopped. In our experiments we studied the case of small Hg drops ($d \approx 10\text{--}50\ \mu\text{m}$) which spread on the surface of the metal Ag. Complete wetting is observed for Hg on Ag surfaces (the contact angle of the liquid drop formed on the solid surface is $\theta = 0$). The spreading of a Hg drop on Ag was observed only on clean metal surfaces. When the surface was left in the open air for an extended period of time (about 30 h for Ag), it was not wetted by the Hg, since the surface was covered by oxides and organic contamination.

Figure 1 presents the overview of the Hg spreading spot on Si substrate after the spreading is stopped as observed by SEM. Figure 1 (a) shows the secondary-electron image and figures 1 (b)–(d) show the characteristic irradiation images for Si, Ag and

Hg, respectively. These figures show that the maximal concentration of Hg was shifted from the centre of the spot at the beginning of the process to about the middle of the radius of the spreading spot at the end of the process. The maximum of Si concentration corresponds to holes, since there the Si substrate is uncovered. As can be seen from figure 1 (*b*), holes are mostly present in the centre of the spot. This is also confirmed by figures 1 (*c*) and (*d*) which show that the Ag and Hg concentrations are low at the centre.

These SEM and optical observations suggest that the observed spreading process exhibits several stages. The first stage is very fast. At this stage the spherical Hg drop transforms to an Hg film circular spot and the spreading is driven by macroscopic surface tension forces. After the transformation of the drop into a circular Hg film, the liquid Hg spreading is driven by local surface tension forces. The liquid Hg phase is found to be present inside the front boundary during the spreading. Hg from the spreading liquid layer reacts with the Ag, penetrates down through the entire film thickness up to about 120 nm and forms thick branches of intermetallic compound γ Ag₅Hg₈ (Hansen 1958). The γ intermetallic compounds were identified by XRD (Joint Committee for Powder Diffraction Standards 1978). The same phase was found in Lee *et al.* (1986). The intermetallic compound forms a net-like structure. The typical area of holes in this net is higher in the centre of the spreading spot. The liquid Hg continues to flow between the intermetallic phase branches.

Shortly after the beginning of the spreading, the liquid film becomes unstable and begins to break. This explosion-like process creates a central area of uncovered glass and many small holes of different sizes in the net of the intermetallic compound in which Hg is absent. This breaking of the liquid film occurs since an energy gain of the spreading and reaction of Hg with the metal is higher than the liquid Hg–air interface energy plus the liquid Hg–glass substrate interface energy; as a result, instability develops. Liquid Hg leaves the centre of the area initially occupied by the drop, leaves the holes in the intermetallic compound net and moves towards the spot rims.

Figure 2 (*a*) shows the optical microscope image in which two fronts are clearly seen. Figure 3 (*a*) shows the TEM image of the thinner Ag film at a higher magnification exhibiting the same property. Between the first (outer) and the second (inner) front, three chemical phases were identified by diffraction TEM analysis: Ag (and Hg solution in Ag); intermetallic compounds (γ -phase); liquid Hg which is present only while spreading is active. Behind the second front, only non-transparent intermetallic compounds and Hg were observed. The roughness and hull analyses were performed only for the outer front.

§4. ROUGHNESS AND HULL ANALYSIS

From optical microscopy observations the front is smooth at the beginning and becomes rougher as the spreading time increases. The roughness exponent increases with time and, when liquid Hg propagation stops (figure 2), the roughness exponent of the front is found to be approximately 1.0 up to a saturation scale $\lambda^* \approx 20 \mu\text{m}$ (figure 2 (*c*)).

In general, a plot of $\ln(w)$ against $\ln(l)$ has three regions. At the very beginning the absence of scaling is due to the lower cut-off length (pixel size) inherent to any digitizing technique. The middle part may correspond to a self-affine (or self-similar) regime and will be linear in the log–log plot with a slope α giving the roughness exponent. In the third region which corresponds to large l values, the roughness

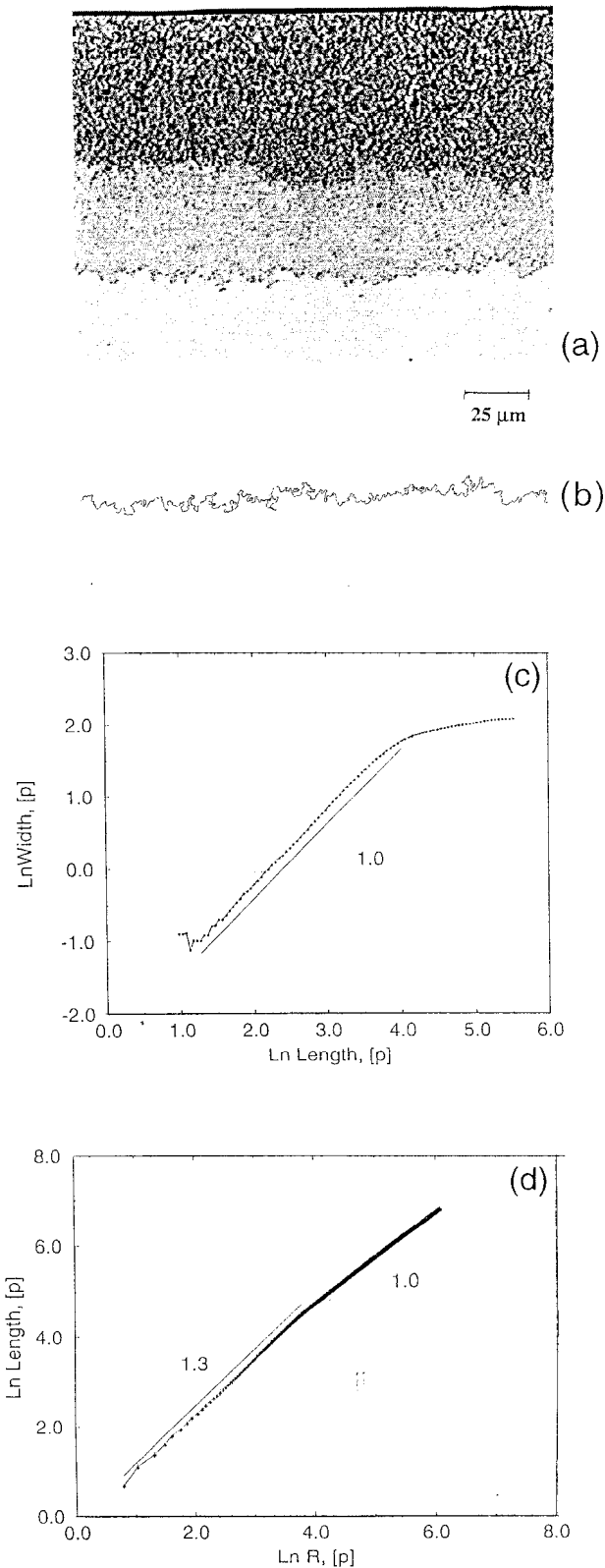


Figure 2. The front observed in the optical microscope at the last front position: (a) optical microscope image; (b) the interface profile found for the interface displayed in (a); (c) the dependence of the interface width $w(l)$ on l in pixels (1 pixel = 375 nm). The roughness exponent (the slopes of the straight line fitted to the data in the middle part) is $\alpha \approx 1.0$. The plateau for large l values $l > \lambda^* \approx 20 \mu\text{m}$ is a result of the $w(l)$ saturation on $w = 5 \mu\text{m}$. (d) The dependence of the interface length $L(R)$ on R (1 pixel (p) = 375 nm). The hull exponent is $\nu = 1.3$, and the saturated part is $\nu = 1$.

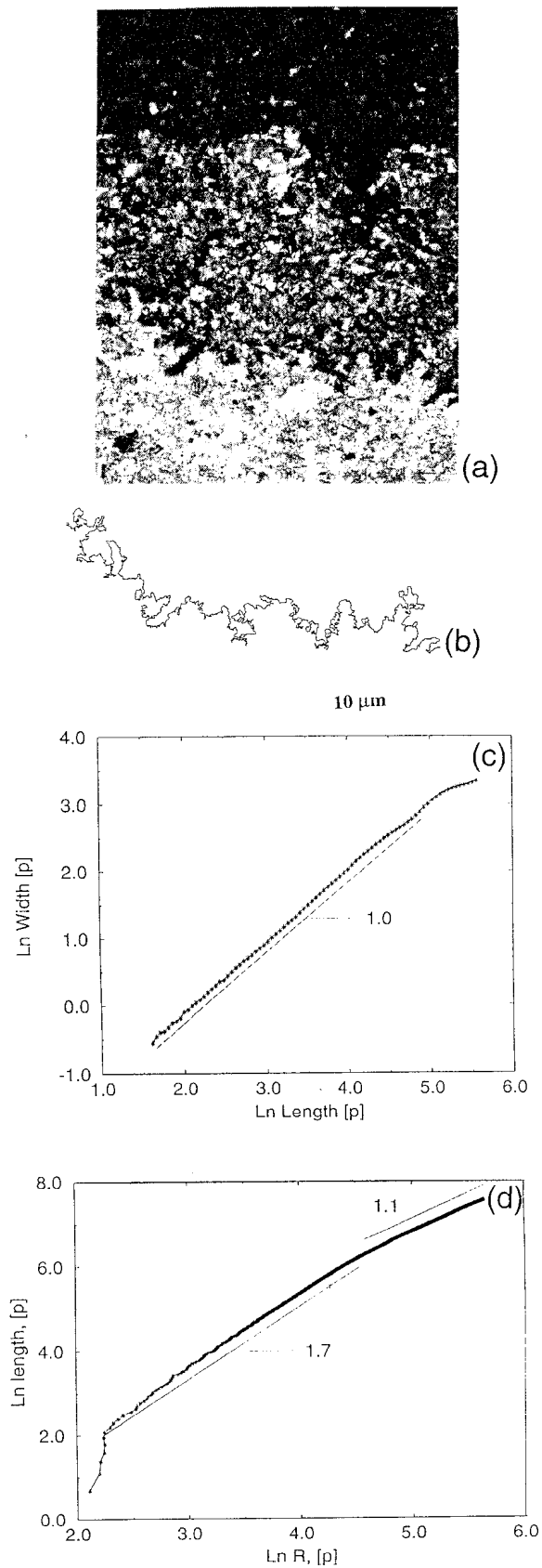


Figure 3. (a) TEM image of the Hg spreading on Ag film 40 nm thick. (b) The interface profile found for the front displayed in (a). (c) The dependence of the front width $w(l)$ on the interval l in pixels (1 pixel (p) = 60 nm). The roughness exponent $\alpha \approx 1.0$ describing the self-affine scaling was determined from the fitting in the middle part. (d) The dependence of the interface length $L(R)$ on the interval R (1 pixel (p) = 60 nm) yields $\nu = 1.7$.

saturates to a constant value. In hull plots the saturation corresponds to a log-log slope equal to unity, which means that the interface is either saturated or self-affine.

Figure 2(c) shows that there exists a wide (0.4–20 μm) range of self-similarity, at which the roughness exponent is $\alpha \approx 1.0$. After a short transition region, α becomes zero and the roughness saturates. The hull exponent calculated for the same image is shown in figure 2(d). In the same initial region (0.4–20 μm) the hull exponent ν is about 1.3 while, for scales larger than 20 μm , ν saturates to approximately unity.

Similar analyses for images of thinner films at a higher magnifications using TEM are presented in figures 3 and 4. These plots show that similar features appear at higher magnification. The roughness exponent $\alpha \approx 1$ and the hull exponent $\nu = 1.6$ –1.7 indicate that the interface is self-similar. These values of the hull exponent are close to those found for hull exponents in a classical percolation model.

Figure 5 shows the TEM picture of the microstructure of the as-deposited Ag film. We see that it contains grains of different sizes (100–800 nm). By digital techniques we extracted different curves which pass through grain boundaries. Two examples are presented in figures 5(b) and (c). We performed the hull analysis for ten curves and found values $\nu = 1.3$ –1.7 for all scales (up to 1.5 μm).

§ 5. DISCUSSION

According to figure 2, one can propose that the front interface can have three levels of roughness. The first is the self-similar formation of Hg islands which gives rise to roughness exponent $\alpha \approx 1$ and hull exponent $\nu > 1$. Those island formations have a finite typical size λ^* (in optical images (see figure 2) $\lambda^* \approx 20 \mu\text{m}$). On the next level the front interface is built up of those islands and the roughness is caused by fluctuations in the position of these islands perpendicular to the interface direction. Those fluctuations may result in a power-law behaviour with a roughness exponent $\alpha < 1$ on a larger scale, that is they may result in a self-affine interface. This can be the case only up to the scale equal to the correlation length λ^{**} at which roughness saturates and remains constant for larger scales. If $\lambda^{**} = \infty$, the interface is exactly self-affine at all scales larger than λ^* .

In our experiments we have not clearly seen a wide region of self-affinity (see figure 2). Rather, the linear regime pass quite slowly to a saturated regime. In the third level the interface is linear and has a typical width which is related to the mechanism. This is reflected in exponents $\alpha \approx 0$ and $\nu \approx 1$. The value $\alpha \approx 1$ and $\nu > 1$ up to saturation obtained for optical and TEM images can be explained by assuming that up to λ^* the front form is self-similar and those self-similar segments are arranged along a line.

In our measurements we obtained values of ν significantly larger than unity. We propose that this may be a result of a percolation invasion-like mechanism of Hg invading the grain boundaries. To test this we performed hull exponent measurements for different trajectories along grain boundaries in a pure Ag film and found that ν values are close to the percolation model values ($\nu = 1.75$). This suggests that up to a certain scale the spreading front simply follows the grain boundaries. The reason for this could be the fact that the grain boundaries are the easiest way for Hg to propagate through the Ag film.

If we assume that grains play the role of a sort of percolation system, then the spreading in it would not result in a finite correlation length. Rather, we observe a quite small correlation length close to the size of the islands, which means that our interface is much smoother than in a simple model of percolation spreading. This is

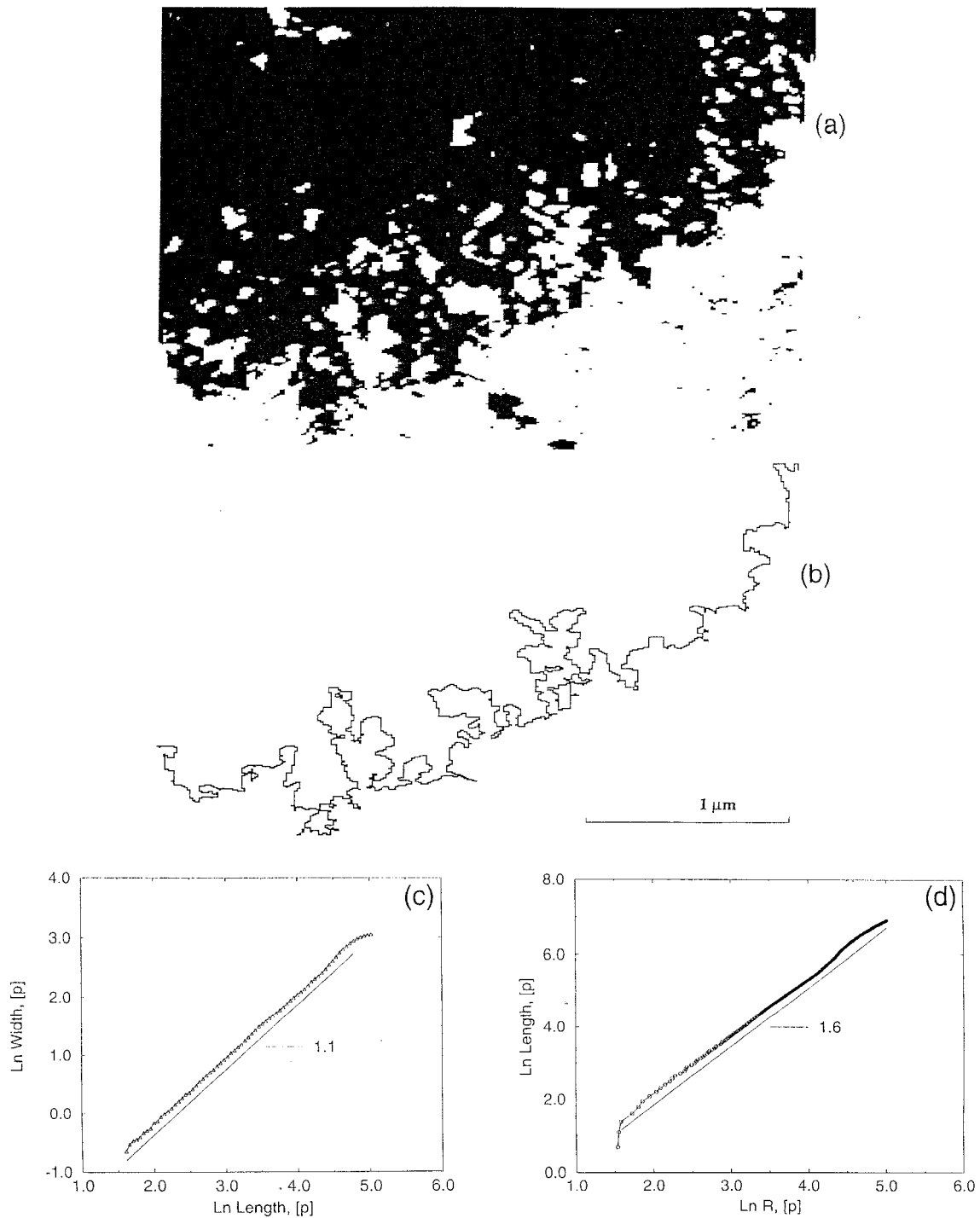


Figure 4. (a) TEM image of the Hg spreading in Ag film 40 nm thick. (b) The interface profile calculated for the interface displayed in (a). (c) The dependence of the interface width $w(l)$ on the length l in pixels (1 pixels (p) = 6.25 nm). The roughness exponent $\alpha \approx 1.0$ was determined from the fitting in the middle part. (d) The hull exponent $\nu \approx 1.6$ (1 pixel (p) = 6.25 nm).

because several mechanisms exist which smooth the interface. The important one is the smoothing by liquid Hg surface tension.

To summarize, the front geometry analyses results suggest that on small scales the interface is self-similar. This can be interpreted in terms of an invasion percolation mechanism. On large scales the roughness of the interface saturates, that is

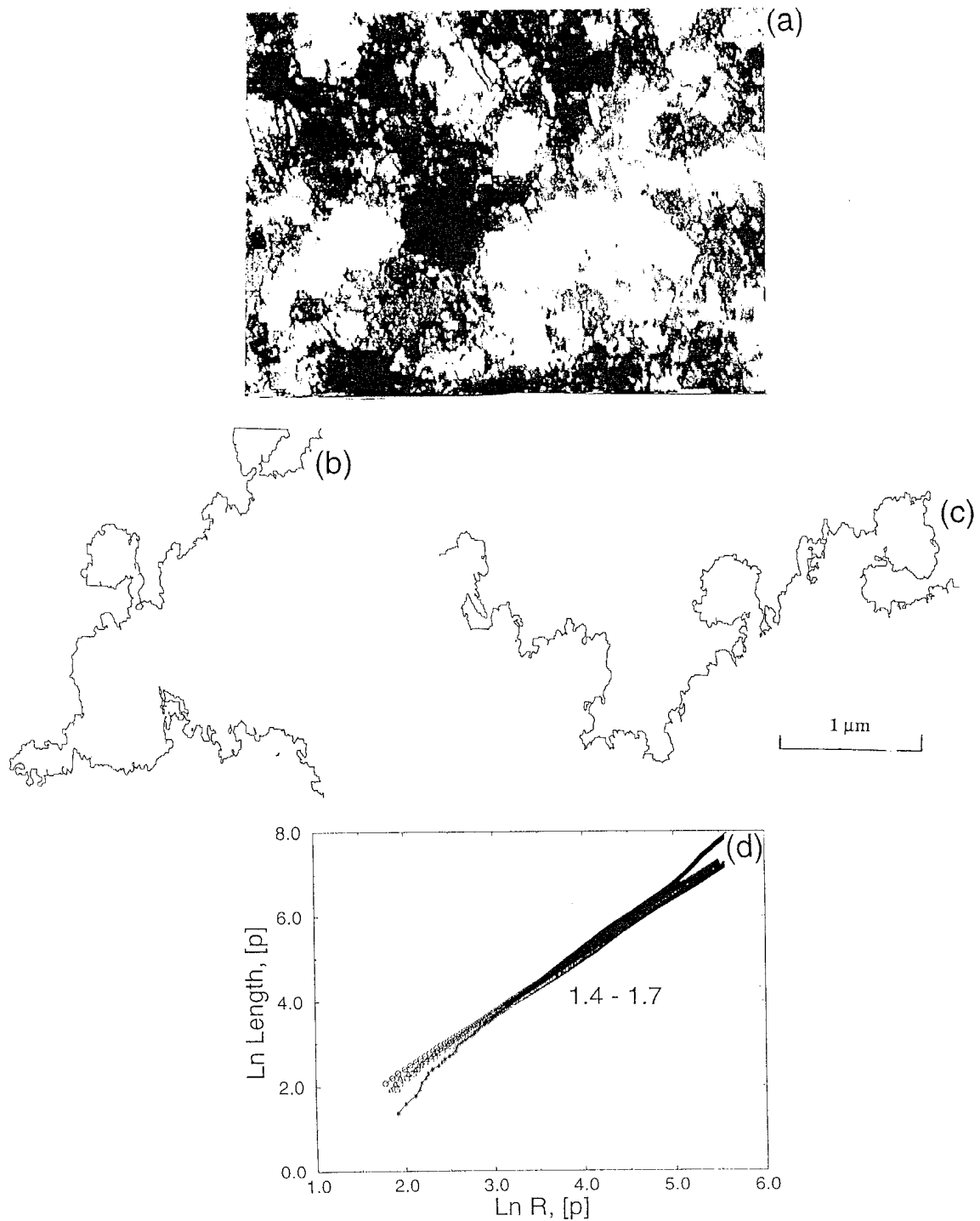


Figure 5. (a) TEM microstructure of Ag film 40 nm thick, not covered by Hg. (b), (c) The different trajectories along the grain boundaries were chosen on pure Ag. (d) The hull exponent of these 'fronts' is found to be in the range 1.4–1.7 (1 pixel (p) = 6.25 nm).

$\alpha = 0$. The physical reason for this roughening could be the fastest propagation of Hg in the grain boundaries in the Ag film.

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