

DETERMINATION OF THE STATISTICAL CHARACTERISTICS OF PORE SHAPE

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In order to optimize processes taking place in porous media, a detailed knowledge of the pore structure is essential. Obviously, the best overall information of this kind of medium is given by statistical functions, which have been used thus far only to measure the radial pore distribution function (or porogram). Nevertheless, this function has two important shortcomings:

1. It does not take into account the shape of the pores, which to a great degree affects the processes which take place in porous media.
2. Most porosimetry methods now in use, mercury porosimetry and capillary condensation, do not offer the possibility of obtaining true porograms for real porous media, either under direct flow (pore filling) or reverse flow. The discrepancy between direct and reverse flow, i.e., capillary hysteresis, can be caused by pore surface irregularity (in the case of both of these methods) and by different meniscus shapes in the same pores (in the case of the capillary condensation method).

This paper presents the results of research on a method for measuring the true pore radial curvature distribution, undistorted by pore shape. It also presents a method for measuring the statistical characteristics of the shape of irregular pores. The contact porosimetry method [1] recently developed was taken as a starting point.

Figure 1a, b, and c show that sequence by which the wetting liquid is removed from the pores by evaporation in contact porosimetry methods and capillary condensation. A similar sequence also takes place in the case of the mercury method. As shown, the front advances to larger pore culs-de-sac only after the meniscus can travel past the restriction of narrower pores. When capillary action occurs (during filling), as in the method of contact porosimetry (see

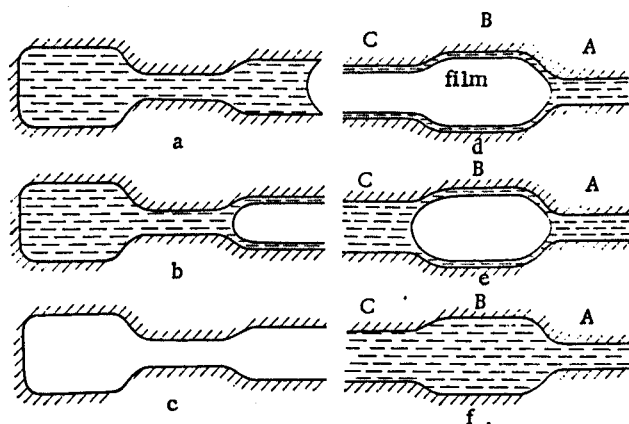


Fig. 1. Sequence of emptying under evaporation (a, b, c) and filling during capillary immersion (d, e, f) in irregular pores.

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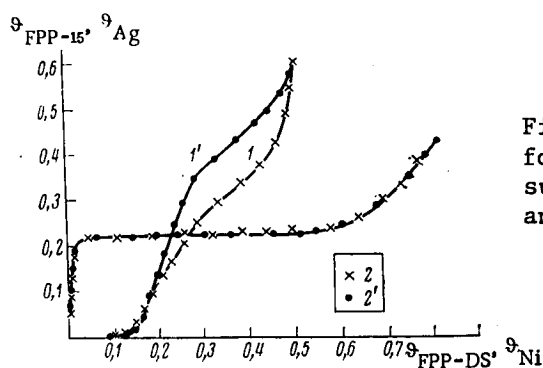


Fig. 2. Curves of moisture transfer during forward (1, 2) and reverse flow (1', 2'), measured for two pairs of specimens of Ag-Ni (1, 1') and FPP-15-FPP-DS (2, 2').

Fig. 1d, e, f), a film of liquid first begins to form on the entire surface and the narrowest pore A is filled. Then, as the liquid overflows in accordance with the pellicular mechanism [2], pore C is filled because it has a smaller radius and therefore also a lower moisture transfer potential [3] than pore B, which in turn is filled at the next stage. We observed such a sequence of filling an irregular pore in an experiment with a glass capillary 1 mm in diameter with an enlargement in the middle. The observed meniscus shape was hemispherical. Two conclusions may be drawn: 1) Capillary hysteresis takes place for curves of relative water content ϑ_1 (ϑ_2) (where ϑ_1 is the ratio of pore volume filled to the total specimen volume) measured under forward and reverse flow by the contact porosimetry method (see Fig. 2, curves 1 and 1') and also for corresponding porograms $\vartheta_1(r)$ (see Fig. 3) for specimens containing irregular pores; 2) the true porogram can be measured from saturation by the contact porosimetry method without neglecting the pore shape. For this purpose, it is essential to have a true porogram as a standard. Inasmuch as such a porogram cannot in general be obtained by any one of these methods, we chose as standards Petryanov filters FPP-DS and FPP-15 [4], in which irregular pores are practically absent. This absence was verified in two ways: First, the coefficients of transfer attenuation $\epsilon = \tilde{\kappa} / \kappa$ (where $\tilde{\kappa}$ and κ are the effective and observed electrical conductivity) turned out to be almost equal to unity for these filters, which agrees with the data of reference [5]. Secondly, hysteresis is absent on curves of the type ϑ_1 (ϑ_2) (see Fig. 2, curves 2 and 2'), which also indicates that the shape of the meniscus for the same blind pores does not depend on the direction in which θ is changing in the contact porosimetry method.

Figure 3 shows the true integral porogram, without neglecting the effect of pore shape (curve 1p), for a specimen of nickel carbonyl.

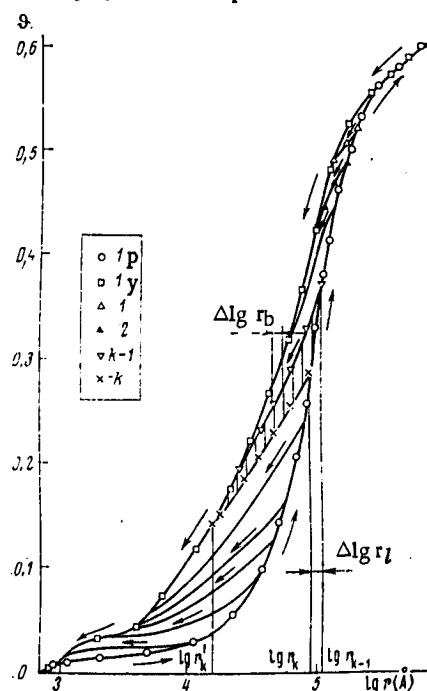


Fig. 3. Integral curves of radial pore distribution measured by the contact porosimetry method, resulting from capillary action (1p), evaporation beginning from complete saturation (1y), and from different degrees of saturation (1, 2, ..., k-1, k...).

The quantitative nature of irregular pores can be most completely expressed by the function $F(r_l, r_b) = \partial^2 \vartheta_l / \partial r_l \partial r_b$, a function of the distribution of the volume ϑ_l of the pores which are blocked (pore traps), based on their radii r_l and radii r_b which obstruct them. To obtain this function an entire family of porograms must be measured. Curves should be included in this family which are measured either by the evaporation method (drying) starting from different stages of saturation $\vartheta_{i,p}$, obtained as a result of saturation or by the saturation method starting from different values of $\vartheta_{i,y}$ obtained by evaporation.

Figure 3 shows a family of experimental integral curves, obtained from the ideal standard FPP-DS, for the same specimen based on the former alternative. Let us consider the method by which the desired function $F(r_l, r_b)$ is obtained starting from these curves. Inasmuch as there are a great many curves of the type $\vartheta_k(r)$, it can be assumed with a sufficient degree of accuracy that the pore culs-de-sac are formed within the radius range $r_{k-1} < r_l < r_k$, the radius interval r_b of the blocking pores is extended from $r_b = r_k'$ to $r_b = r_k$, where r_k' is the pore radius corresponding to the point of intersection of curve k with curve l . The volume distribution function of pore culs-de-sac in the radius range from $r_l = r_k$ to $r_l = r_{k-1}$ is determined for values of r_l and r_b by the expression

$$F_{(k-1),k}(r_l, r_b) = \frac{[\vartheta_{(k-1)}(r_b + \Delta r_b) - \vartheta_{(k-1)}(r_b)] - [\vartheta_k(r_b + \Delta r_b) - \vartheta_k(r_b)]}{\Delta r_b \Delta r_l}, \quad (1)$$

where $\Delta r_l = r_{(k-1)} - r_k$ and Δr_b is the low value of the variance in radii of the blocking pores in the range $r_b = r_k'$ to $r_b = r_k$. In this way we obtained an expression for determining the desired function $F(r_l, r_b)$. Figure 4 shows function $F^*(\log r_l, \log r_b)$, analogous to function $F(r_l, r_b)$, obtained from Fig. 3 in the manner described. Lines are constructed, similar to those shown on that figure, of the quantity $F(\log r_l, \log r_b)$ with the dimension of $(\mu m)^{-2}$ on coordinates $\log r_l$ and $\log r_b$. Information about the structure of the specimen under study, contained in Fig. 4, is very extensive and complex. Here we present only a few conclusions:

All the pores of a specimen can be classified into three types: 1) coarse, slightly irregular pores with a radius greater than 10 μm , formed by blowing agents; 2) moderately irregular pores ($r = 2-15 \mu m$) between grains of nickel carbonyl measuring 10-20 μm ; and 3) the small volume of fine, slightly irregular pores with radius less than 1 μm inside the very fine particles of nickel carbonyl. All these data agree with other information on the structure of specimens under study.

Thus, information contained in the function $F(r_l, r_b)$, other than information available from a conventional program, makes it possible to depict the shape of pores of various types and also their relative distribution in different elements of the solid structure framework; that is, it makes a quantitative formulation of the real structure model of a specimen possible.

The authors express profound thanks to V. S. Bagotskii for this discussion of this paper.

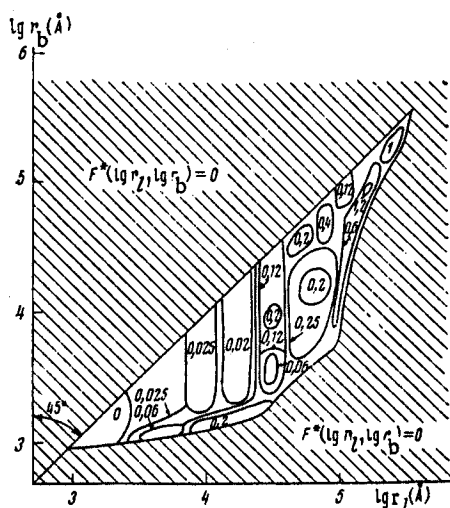


Fig. 4. Volume distribution function of blocked pores expressed as the logarithm of their radii and the logarithms of the blocking radii.

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SECONDARY ELECTRON EMISSION OF AN IRIDIUM SINGLE CRYSTAL

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There are data in the literature on the anisotropy of the secondary electron emission of single crystals of body-centered-cubic metals: tungsten [1], molybdenum [2], niobium [3], tantalum [3], and iron [4]. The secondary-emission properties of face-centered cubic metals have been studied only for the (111) plane of a nickel single crystal [3].

The aim of this work is to study the anisotropy of the secondary electron emission coefficient (s.e.e.c.) σ and the inelastic reflection coefficient (i.r.c.) η on the (100), (110), and (111) planes of an iridium single crystal, having a face-centered-cubic lattice. An iridium single crystal 8 mm in diameter and 100 mm long was grown by electron-beam zone melting in vacuum after three passes of the zone through the sample. Experimental samples of a given orientation with dimensions $6 \times 10 \times 1$ mm each were cut by electroerosion and polished mechanically and electrolytically. The quality of the samples was checked by microstructural and x-ray methods. The deviation of the plane of the surface of the samples from a given crystallographic plane did not exceed 1° .

For the (100), (110), and (111) planes of the iridium single crystal at primary electron energies $E_p = 60-2000$ eV, the $\sigma(E_p)$ and $\eta(E_p)$ dependences presented in Fig. 1 were obtained. The measurements were made in a vacuum of 10^{-10} torr at room temperature at energy intervals of 20 eV after heating the samples at 2000°K for 25-30 h, at which time the s.e.e.c. and i.r.c. values of all planes were stabilized. The accuracy of the determination of σ , η , and E_p was 0.3-0.5% [5].

Both the s.e.e.c. and the i.r.c. are characterized by significant anisotropy, which is shown by the differences in the $\sigma(E_p)$ and $\eta(E_p)$ dependences for the different crystallographic planes. The $\sigma(E_p)$ and $\eta(E_p)$ dependences have distinct structure in the form of a system of maxima and minima. The positions of the structural elements depend on the crystallography of the plane being studied. However, the positions of the extrema on the $\sigma(E_p)$ and $\eta(E_p)$ curves for each of the planes coincide. For the (100) plane, the s.e.e.c. value exceeds 2.0 in a broad energy range, which does not occur for any element in the polycrystalline state at normal incidence of the primary electrons.

In [1, 2] a separation of the nonmonotonic features into two types was proposed. Structures of the first series include maxima and minima as well as "steps" of the order of several hundred electron volts. Analogous nonmonotonic features, but having widths of the

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