Scale Factor upon the Grain Boundary Wetting in Polycrystals

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Abstract—The intergrain penetration of wetting liquids (water and gallium) is studied with polycrystalline samples of NaCl and zinc, respectively. A strong effect of a scale factor is found. The quantitative correlation between the results of simulation and the data of physical experiments is established and is indicative of the applicability of the percolation theory to describe the process of intergrain wetting.

INTRODUCTION

Solids containing liquid inclusions represent a class of disperse systems, which must be studied both to develop a number of technological processes and to analyze most of the geological phenomena. Among the parameters determining the properties of such heterophase materials, the prime importance often belongs to the degree of connectivity of liquid inclusions, which can be efficiently estimated using the mathematical apparatus of the percolation theory. In particular, the application of this theory to describe the grain boundary wetting in polycrystals was proposed elsewhere [1–3]. The development of this line of research, like any application of the percolation theory to physical objects, requires to account for their finite size, since the precise values of percolation thresholds $p_c(\infty)$ and other fundamental percolation parameters refer to infinite spaces or half-spaces [4]. Theoretical works, which make it possible to estimate the role of scale factors, constitute a small fraction of the total number of works on the percolation theory and their results are often contradictory.

The scale effect upon two-dimensional invasive percolation along the square lattice can be clearly demonstrated using the following simplest computer simulation. A square filled with randomly distributed (with a frequency of p) pixels of the same color is created on the computer display and then black color is spread across the pixels beginning with one side of the square. If a rather dense $(p > p_c(\infty) = 0.59275)$ network of pixels is created and the square is large enough, a cluster of black elements reaches the opposite side (Fig. 1a). However, if the same square is cut into thin strips L pixels in width and *nL* pixels in length, some tortuous ways of transfer will be cut off (Fig. 1b). It is obvious that the color will reach the opposite side of the strip, provided that $p \ge p_c^{(n)}(L) > p_c(\infty)$ (hereafter, $p_c(L)$ and $p_c^{(n)}(L)$ values will designate the percolation thresholds on the lattices consisting of $L \times L$ and $L \times nL$ sites, respectively). It should be kept in mind that, even for this simplest computer experiment, the stochastic distribution of the elements of the percolation lattice (pixels) must be strictly adhered to: when the correlation is present (for example, the anisotropy of clusters), the experiment can fail.

Polycrystals brought into contact with liquid which can propagate along the grain boundaries demonstrate a similar behavior. Thus, in a NaCl–water system, a network of wetted grain boundaries can be spread for tens of kilometers (in salt beds) or terminated at the distances comparable with the size of laboratory samples.

To differentiate the scale effect between many factors controlling intergrain wetting, this effect must be described quantitatively, as well as compared to percolation models and/or to theoretical predictions, provided that the stochastic distribution of elements is met. In this work, such an attempt was taken with Zn–Ga and NaCl–H₂O systems.

EXPERIMENTAL

Dependence of the Permeability of Grain Boundaries on Their Disorientation in Zn–Ga and NaCl–H₂O Systems

At the first stage of the investigation of the above systems, we attempted to find the correlation between the permeability of the grain boundaries and their disorientation as a parameter whose stochastic distribution can be experimentally verified using common methods of the texture analysis.

Zinc granules (99.95% pure) were subjected to cold rolling and then cut into strips $30 \times 15 \times 0.6$ mm³ in size. After annealing for 30 h at 350°C, the average grain size was 40 µm. The samples were wetted along the perimeter with liquid gallium (99.99% pure) preliminar-



Fig. 1. The role of the sample width upon the invasive percolation on the square lattice (computer simulation): (a) the black cluster is spread throughout the sample or (b) stops at a short distance from the source, if the sample is cut into strips.



Fig. 2. The relative number of wetted grain boundaries in polycrystals n/n_0 as a function of the angle of grain disorientation θ for (a) Zn–Ga and (b) NaCl–water systems.

ily saturated with zinc and aged at 40°C for 72 h. The presence of gallium at grain boundaries was recorded with a JSM 6400 scanning electron microscope equipped with an X-ray analyzer and the resulting maps of gallium distribution were compared with the maps of grain disorientation obtained with a ZEISS DSM-940 electron microscope using diffraction of backscattered electrons. No predominant orientation of grains in the zinc strips was observed. The probability of the grain boundary wetting grows monotonically with the disorientation angle θ (Fig. 2a) and, at 30° < θ < 90°, the probability is equal to ~0.8.

The intergrain wetting in a NaCl-H₂O system was studied using salt polycrystals with an average grain size of 300 μ m. The samples 20 \times 30 \times 5 mm³ in size were prepared by pressing single crystals at 650°C followed by annealing at 500°C for 6 h. To construct disorientation maps, a special procedure was developed. The sample was wetted by a saturated aqueous NaCl solution and subjected to fast drying. In this case, pyramidal crystals with inherited grain crystallographic orientation and limited by {100} planes were deposited onto each grain. A polycrystal was placed on the Fedorov stage and was illuminated by a narrow light beam at a fixed angle. By establishing the polycrystal position corresponding to the maximum intensity of reflection from each grain, its orientation can be easily determined. The distribution of grain boundaries over disorientations appeared to be close to the distribution typical of randomly disoriented ensembles [5]. The grain boundaries wetted at prolonged contact with solution (several hours) were well observed with an optical microscope. In this system, the probability of grain boundary wetting also grows monotonically with the disorientation angle reaching ~0.8 at θ > 40° (Fig. 2b).

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Experimental Study of Scale Effect upon Intergrain Wetting

Using the strips of zinc foil different in width, the distances H of gallium penetration along the network of grain boundaries were measured. To prepare samples of this series, zinc was rolled to the foil 60 μ m thick; the

mean grain size \overline{d} after annealing was equal to $85 \pm 8 \,\mu\text{m}$. According to X-ray diffraction analysis, there are no internal stresses in the samples. A gallium droplet with a mass significantly exceeding the value necessary for wetting all grain boundaries in the sample was smeared on the narrow end of a strip. The sample was allowed to stand at 40°C for several days and then was frozen in a liquid nitrogen. Two days were usually sufficient to terminate the gallium front propagation The analysis with a scanning electron microscope showed that, in the wetted portion of the sample, gallium is located along 60– 65% of the grain boundaries and is practically absent on the outer grain surface.

In other series of experiments, we used zinc (technical grade) with $\bar{d} = 300 \,\mu\text{m}$. The position of the gallium propagation front was determined as follows: the strip was indented facing the side opposite to the gallium source; the appearance of microcracks indicated that the indenter reached the wetted portion of the strip. Statistical differences between two series of experiments were not found, hence, Fig. 3 (curve *I*) presents the unified data (for a total of 127 samples).

The scale effects of water penetration were studied with cylindrical sodium chloride polycrystals 4.5 mm in diameter and 10 cm in height. The samples were prepared by the extrusion of single crystals heated to 600°C followed by the recrystallization at 430°C; the mean grain size amounted to 350 µm. The sample end was placed in a saturated aqueous salt solution containing small amount of LiCl. The electric conductivity of a NaCl polycrystal at its parts with wetted boundaries significantly exceeded the conductivity of dry material and was equal to $(5.2 \pm 0.9) \times 10^5 \Omega^{-1} \text{ m}^{-1}$. As the intergrain penetration was completed, the sample was divided into parts; the content of lithium in each part was determined by atomic absorption spectrometry and the amount of water at the grain boundaries was calculated depending on the distance from the source (Fig. 4).

COMPUTER SIMULATION: METHODS AND RESULTS

The grain boundary wetting was simulated as a site percolation problem on a square lattice (the applicability of such a model to describe a quasi-two-dimensional grain boundary network was discussed in [3]). The permeable and impermeable elements were randomly distributed over the network sites with the probabilities of p and 1 - p, respectively. The strips of zinc foil with the width of L grains were simulated by a matrix containing L columns and nL transverse rows. The process of the

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Fig. 3. (1) The length H of liquid gallium penetration into the zinc foil strips vs. their width L and (2) the results of computer simulation of percolation on the square lattice.

propagation of liquid across the strip from the source located along its end was simulated as a transformation of a permeable element into a wetted element in each subsequent row, provided that this element is in contact at least with one wetted element in a row or a column.

Note that the results of laboratory experiments are in a good agreement with the results of computer simulation, if the number of experimental points in the latter case is also limited by several tens (Fig. 3, curve 2). To obtain the reliable $p_c^{(n)}(L)$ values and establish their correlation with the universal critical exponents [4], we carried out approximately ~10⁵ computer experiments varying the sample width L from 3 to 20 columns and the probability p from 0.6 to 0.85.

DISCUSSION

Dependence of Wetting Probability on Disorientation Angle

As was confirmed in [6, 7], the grain boundary wetting in both systems studied is uniquely due to a reduction of the interfacial free energy upon wetting. Hence, the construction of adequate percolation models of grain wetting requires direct evidences of the random character of the grain boundary energy distribution. Strictly speaking, one cannot exclude the presence of some correlation effects (e.g., a local increase in the chemical potential of a solid due to the stresses that arise upon the penetration of a liquid), which can additionally affect the grain boundary wettability. Thus, we can only state the quasi-random character of the grain free energy distribution.

The correlation between the percolation and the grain boundary energy could be implicitly followed by comparing the geometric parameters of dry and wetted boundaries. An adequate correlation between these values was established for a Fe–30%Mn–10%Cu–Cu melt



Fig. 4. The probability P_n of the penetration of a liquid to distance *H* from the source as a function of n = H/L by the results of experiments with (*1*) cylindrical NaCl polycrystals with diameter *L* and (2) computer simulation on the prisms with base $L \times L$.

pair [8]. A model proposed in [8], where the grain boundary energy is represented as a function of five macroscopic degrees of freedom, makes it possible to predict that 80% of grain boundaries are wetted. In this system, the correlation between the wettability of the grain boundary and the angle of its disorientation turned out to be very weak that was explained in [8] by the presence of many special boundaries in solid phase.

In Zn–Ga and NaCl–water systems, a much more clear correlation between one degree of freedom (disorientation angle θ) and the permeability was established (Fig. 2). In this case, the special boundaries seemingly have no marked effect (in any case, at each selected step of histograms). Thus, for these systems, the conclusion on a random character of the distribution of permeable grain boundaries can be made by measuring θ angles to clarify the presence or absence of the predominant grain orientation (texture).

Percolation Parameters Determined in Laboratory and Computer Experiments

The precise quantitative interpretation of the relation between $p_c^{(n)}(L)$, *n* and *L* suggests the critical analysis of works performed in this field of research, because there is still no universal theoretical model. It turned out that, for our data, the most applicable was the expression taken from [9] and describing the scale effect

$$p_{c}^{(n)}(L) - p_{c}(\infty) = L^{\frac{1}{\nu}} \left[(C_{1} + C_{2})(\ln n)^{\frac{1}{\nu}} \right], \quad (1)$$

where C_1 and C_2 are constants and v is the universal critical exponent of the correlation radius which is independent of the lattice type and is equal to 4/3 and to approximately 0.88 for two- and three-dimensional space, respectively.

Indeed, the data of our computer experiment on the propagation of the liquid front along the strips with different widths are well linearized in the $(\ln n)^{1/\nu} = f(p_c^{(n)}(L))$ (Fig. 5) coordinates and the straight lines converge in point $p_c^{(n)}(L) \cong 0.59$ close to the known value of percolation threshold $p_c(\infty) = 0.592746$ in the site percolation problem on the square lattice. Strictly speaking, the resultant points of intersection with the abscissa must lie in the $p_c(\infty) + 0.11C_1 < p_c(L) < p_c(\infty) + 0.35C_1$ range whose width is much smaller than $p_c(\infty)$. In other words, the difference between $p_c(\infty)$ and $p_c(L)$ for the square $(L \times L)$ and, probably, cubic $(L \times L \times L)$ samples can be neglected compared to the difference in $p_c(\infty)$

and $p_c^{(n)}(L)$ for elongated strips (prisms).

Figure 6 demonstrates a further proof of the correlation between the results of model experiments and Eq. (1): the slope of straight lines in Fig. 5 changes linearly with the $L^{-1/\nu}$ value.

Thus, Eq. (1) describes excellently the results of model experiments which, in turn, are in a good agreement with the data obtained for real quasi-two-dimensional polycrystals (under the condition that the average value H = nL is a median rather than the expectation). However, Marrink and Knackstedt [9] indicate that their model is rigorously applicable only at n > 1. An approach applicable to low n values (up to n < 1) was developed in [10]. In this case, the dependence of the percolation threshold on the sample size is set by the equation

$$H^{-1/\nu} - L^{-1/\nu} + p_c^{(n)}(L) = p_c(\infty).$$
⁽²⁾

The substitution of the computer simulation data in the left-hand side of Eq. (2) gives the value which is practically constant beginning with L = 6 and close to the true percolation threshold for the site percolation problem on the square lattice, $p_c(\infty) = 0.59275$ (Fig. 7a).

As to the experiments with a zinc–gallium system, it should be keep in mind that the v exponent is invariant for all two-dimensional cases, and the $p_c(\infty)$ value depends on the specific geometry of the percolation problem. In particular, if the grain boundaries in a thin foil are used as elements, the situation is reduced to the bond percolation problem on a honeycomb lattice.

The results of experiments with the zinc foil presented in the same coordinates as for the computer model strongly support the proposed scheme (Fig. 7b). As for the computer model, the experimental dependence is approximated by horizontal line $p_c^{(n)}(L) = 0.66$; however, in this case it lies near the percolation thresh-

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Fig. 5. The correlation between the n = H/L value and percolation threshold $p_c^{(n)}(L)$ (the results of computer simulation on two-dimensional lattice at different *L* values).

old for the bond percolation problem on the honeycomb lattice, $p_c(\infty) = 0.65271$.

Analysis of the Experimental Data Obtained with Three-Dimensional Samples

The percolation approach was applied to describing the properties of grain boundary ensembles wetted by water upon its penetration into the cylindrical NaCl polycrystals.

The ratio of the values of bulk electric conductivity measured for wetted NaCl polycrystals and the conductivity of a saturated aqueous sodium chloride solution is equal approximately to 2×10^{-6} . If, according to [1], the fraction of permeable grains in a NaCl polycrystal is $p \cong 0.3$, then at the thickness of liquid interlayer of $\ge 0.1 \ \mu m$ and the mean grain size of 300 μm , this ratio should be $\ge 2 \times 10^{-4}$. The difference by two orders of magnitude can be explained only in terms of percolation theory. In fact, above the percolation threshold, most of the continuous network of liquid interlayers is due to the so-called "dead ends" of a cluster rather than to its "skeleton" which is responsible for the conductivity. In the vicinity of the percolation threshold, the conductivity is approximately proportional to the $(p - p_c)^{\mu}$ quantity, where critical exponent μ is equal to 2 (for 3D lattices) [4]. In case of the grain wetting of polycrystals, the theoretical estimation of the percolation threshold is equal approximately to 0.2 [1]; hence, $(p - p_c)^{\mu} \cong 0.01$ that can explain the observed difference.

A decrease in the water content along the NaCl samples wetted from the end (Fig. 4) can be interpreted as a decrease in the density of a percolation cluster typical of elongated $L \times nL$ lattices. The P_n value (the probability that, at $p > p_c(\infty)$), the growing cluster will reach the

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Fig. 6. The slope of lines presented in Fig. 5 as a function of the strip width.



Fig. 7. The values of percolation threshold obtained from the results of (a) computer simulation (the site percolation problem on the square lattice) and (b) the laboratory experiment with the Zn–Ga system.

remote end) decreases exponentially with an increase in n [9]. Note that the density gradient is difficult to follow in the single laboratory or computer experiments; however, an increased number of experiments makes it possible to obtain the linear dependence of the averaged value $\ln P_n$ on n with rapidly increasing correlation coefficient. A simple relation proposed for large p and n values is given in [9]. This relation can be written in the following form:

$$\ln P_n / \ln P(L) = 2n - 1, \tag{3}$$

where P(L) is the probability of percolation on the square $L \times L$ or cubic $L \times L \times L$ lattices. The data on simulation presented in Fig. 4 demonstrate the validity of Eq. (3) even for not too large $p - p_c(\infty)$ and *n* values and suggest that this equation will be applicable to

study the scale factor in the processes of grain boundary wetting.

The first attempt of using this approach to explain the behavior of the NaCl-water system was successful: the experimental data were in a good agreement with the results of computer simulation. However, to estimate the reliability of the above correlation, a high sensitivity of the slope of the calculated curves to the accuracy of P(L) measurements (the infinite scatter at $P(L) \longrightarrow 1$) should be taken into account.

CONCLUSIONS

In spite of the fact that the applicability of the percolation theory to the description of the grain boundary wetting in polycrystals seems to be evident, the violation of some conditions (the disregard for the latent correlations and scale factor) can lead to erroneous estimates. This work manifests the adequacy of the percolation models used, at least, for two systems, Zn-Ga and NaCl-H₂O. As applied to these systems, the following main conclusions can be formulated: (1) the reliable correlation between the grain boundary permeability and the disorientation angle was found that is indicative of the random character of wetted boundary distribution in nontextured polycrystals; (2) the dependence of the wetting front propagation in quasi-twodimensional zinc polycrystals on their width correlates with the computer model and is described using the percolation constants; (3) the interpretation of the measured values of the conductivity of wetted NaCl polycrystals is possible only with allowance made for the topology of the percolation cluster of wetted boundaries; and (4) a decrease in the content of water along the line of its penetration into the cylindrical NaCl polycrystals agrees with the percolation model.

The results obtained make it possible to state that the applicability of the percolation theory to the description of intergrain wetting was confirmed experimentally for the first time.

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