PERCOLATION APPROACH TO GRAIN BOUNDARY WETTING: THEORY, COMPUTER SIMULATION AND EXPERIMENT

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ABSTRACT

Grain boundary wetting in polycrystals is analysed as a percolation process. Percolation theory provides mathematical tools which can be used for predicting certain macroscopical properties of internally wetted polycrystalline materials: percolation threshold, topology of wetted (or dry) boundaries ensembles, finite size effects etc. In this paper, we discuss advantages and difficulties connected with the percolation approach.

INTRODUCTION

A large amount of literature deals with percolation theory and its applications (see, e.g. [1]) describing the behaviour of various systems having a common feature: they are constituted of elements (sites and bonds linking them) characterized by a randomly distributed parameter responsible for their connectivity. Percolation theory postulates the existence of a sharp transition (percolation threshold p_c) at which the long-range connectivity of the system (an infinite cluster of connected elements) appears (or disappears) when the occupation probability p of an element gradually increases (or decreases). Wetting of grain boundaries (GBW) in polycristalline materials may be considered as a percolation process because of the difference (stochastic at least in some cases) in wettability from one boundary to another. In this paper, we develop our previously reported [2,3] work laying an emphasis on some new experimental evidence confirming theoretical predictions.

THEORETICAL PREDICTIONS

We shall firstly analyse the simplest case of GBW in an imaginary ideal polycrystal. Consider an array of identical polyhedral grains having a constant number of faces per cell (e.g. $F = 12$) and sides per face (e.g. $S = 5$) and let a given boundary (or another polycrystal element) be wettable at random, i.e. the wetting probability of each element p is assumed to be independent on the fact whether the neighbour element is wetted or not. Even this simplified picture allows us to make some quantitative estimates.

1. Percolation thresholds Values for p_c can be found from coordination numbers z (number of percolation lattice elements contacting any given element): either as well-known solutions for classical percolation problems of both types (site or bond) on regular 2D and 3D lattices with the same z, or interpolating such values. Some examples are given in Table 1.

One can see that the percolation thresholds are scattered over a rather wide range, as a function of the system geometry. So, for p lying between 0.2 and 0.65, the wetting path should be considerably shorter in one-grain-thick foils than in 3D specimens. Cases 1,3 and 5 refer to different percolation sub-systems within the same 3D structure. It should be noted that while p_c values can be inferred from purely geometrical considerations, the underlying p values

become interrelated if we attribute to them a physical (interface energy based) meaning, as it is generally accepted (see detailed analysis in [3]).

Table 1.

N°	Wettable element	Lattice	D	z	Type	p_c
1	GB plane in a 3D polycrystal	f.c.c. - b.c.c.	3	10	site	0.21
2	GB plane in a thin foil	honeycomb	2	3	bond	0.65
3	Triple junction line	diamond	3	4	bond	0.37
4	GB plane on a fracture surface*)	triangular	2	6	site	0.50
5	GB plane + wettable corners	-	3	15	site	0.18

*) We have analysed percolation on a facetted surface for various values of S; here for simplicity's sake $S = 6$.

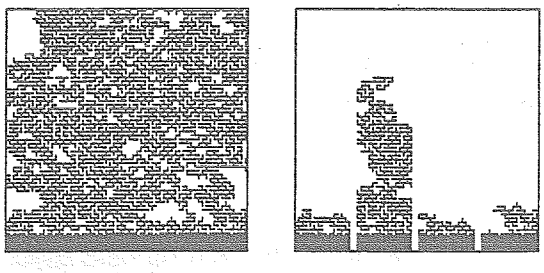
2. Fractal structures Certain parameters X characterizing structure, transport and some other properties of percolation clusters are known to depend only on the dimensionality of the system and not on the coordination number. Therefore they are predictable with a greater deal of reliability than p_c . In general, a set of universal critical exponents y defines such properties not too far from p_c :

$$X \sim | p - p_c |^{y}$$

In particular, these exponents determine the fractal topology of percolation clusters characterized by the correlation length ξ and the effective Hausdorff fractal dimensionality d. Thus, near p_c the amount of the liquid phase M in wetted GBs should be related to their size R not by usual Euclidean relationships, but by $M \sim R^d$ with $d = 1.90$ in 2D and 2.5 in 3D cases. At $p > p_c$, the infinite network of wetted GBs should scale over about one order of magnitude at lengths less that ξ , and it is homogeneous above ξ . For isolated finite clusters of wetted GBs at $p < p_c$, d = 1.56 or 2 in 2D or 3D respectively.

We have computed fractal dimensions of model 2D finite and infinite clusters in order to establish the minimum number of points required for obtaining reliable values. Several hundreds of points usually are sufficient for an accuracy of $\pm$ 0.01.

3. Finite size effects The applicability of the theoretical percolation approach crucially depends on the size of the system. Finite size effects in invasion percolation are illustrated in Fig.1 a,b: the model "wetting liquid" ascends along "GBs" at $p = 1.1\ p_c$ in a different manner in two identical samples, one of which is cut into four narrow strips. The critical probability of the finite system p_c^* is here (b) considerably higher than its value for an infinite system. Generally, $p_c^* > p_c$ for narrow samples and $p_c^* < p_c$ for short ones.



a b

Fig.1. Computer simulation of 2D invasion percolation on honeycomb lattice: role of the sample width

True values of p_c can be found from experimentally determined p_c^*, using scaling laws relating these values with universal critical exponents. Use of finite size samples is a very

promising method for solving various percolation problems (see e.g. [4]). Explicit relationships are given in [5] for samples with a constant length to width ratio.

4. Correlated and oriented percolation problems Many percolation problems deal with not completely random systems where the occupation of a site or a bond may influence the occupation of its neihgbours [6], or the probability p depends on space orientation of the bond [7]. In the context of the present work, a number of situations arises when the correlation or orientation effects are to be taken into account:

4.1. Polychromatic percolation In two-phase systems, three kinds of grain boundaries AA, BB and AB have generally different wettabilities p_{IJ} and, obviously, are disposed in a non-random way. As we have shown using renormalization group method and direct computer modelling, p_c may be lower or higher than the usual z-defined value, but the difference is negligible excepting some special situations. So, if the wetting probabilities in a 2D square lattice are $p_{AA} = p_{BB} = 0$ and $p_{AB} = 1$, i.e. every adhesive and no one cohesive boundary is wetted, then p_c is lowered by about 0.05.

4.2. Grain misorientation A correlation factor inherent to polycrystals is the grain misorientation angle θ influencing, as it is known, the wetting probability of any given GB. We have studied the role of this factor for various 2D and 3D computer models of polycrystals by comparing experimental p_c values (found as percolation probability P = 50%) for randomly distributed θ and correlated θ computed from orientations of neighbouring grains. The difference has been found to decrease sharply with increasing coordination number and to have a maximum value (about 0.02) for thin polycrystalline foils (Fig.2). Such a method enables us to model percolative properties of texturized materials, provided that p (θ) dependence is known.

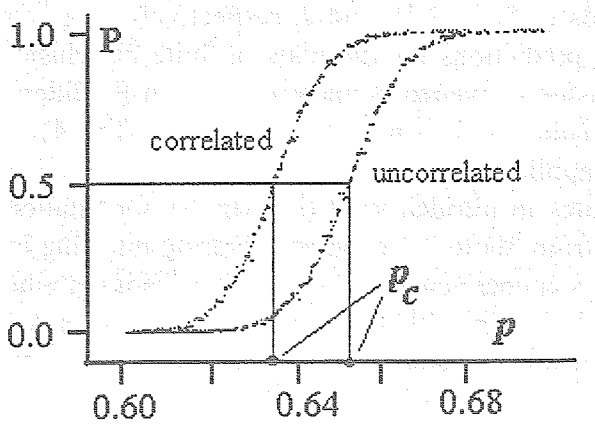


Fig. 2. Percolation threshold shift as a result of the correlated character of grain misorienation in a model honeycomb lattice

4.3. Oriented percolation Oriented GBW in a stressed model polycrystal was firstly theoretically studied in [8]. It can easily be seen that in a stress field enhancing or inhibiting GBW along certain directions, an anisotropy of p_c should exist, which can lead finally to a transition from 3D to 2D geometry implying a p_c increase (cf. cases 1 and 4 of the Table 1). We have estimated p_c in a quasi-2D facetted surface generated by such a transition, over a range of <S> (average GB polygonality) and shown that for 5 to 6-sided GBs, a p_c increase should be more than twofold.

EXPERIMENTAL

There are many reasons why the above outlined approach can supply good or not very good models for various real polycrystalline materials. At least two questions are vital in each

concrete case: what value can we take for z, and is p really constant throughout the polycrystal? The first question does not create serious difficulties because the results exemplified in Table 1 are easily extendable to any other z. Moreover, the low z values are usually well defined, while for high ones p_c is less sensitive to z variations. As for the second question, the answer can be very informative: the extent to which experimentally observed GBW obeys the percolation laws, as well as the fractal dimension of GB ensembles, may be regarded as a criterion for its stochastic character and thus to provide an insight into the physico-chemical mechanism(s) of the process.

As in many other applied percolation problems, exact **percolation thresholds** cannot be determined experimentally. However, there is an abundant evidence confirming that continuous or discrete topology of wetted GB clusters is determined as stated above, at least at $p << p_c$ or $p >> p_c$. For example, we observe a dramatic difference in wetting path length in 3D and quasi-2D polycrystals Zn-Ga, NaCl-H_2O and many other couples.

More exact estimates can be obtained by studying **finite size effects** which were already reported [2] for NaCl cylindrical polycrystals wetted with brine. We have studied more extensively GBW of a thin foil of Zn by liquid gallium. The results are shown in Fig.6. Comparing experimental plot to computer models confirms the percolative character of the process: the shapes of experimental and computer curves are similar, as well as experimental wetting probability (0.6 to 0.65 as directly measured using SEM technique) and model values.

A direct experimental evidence for the **fractal character** of GBs ensembles (and, consequently, for the applicability of the percolation ideas) has been obtained by measuring misorientation angles for a great number of GBs and topology of Ga-wetted GBs clusters in Zn polycrystals (Figs 3 to 5). Zn-Ga system has the advantage of having a wetting probability (about 0.6 in our experiments) close to p_c for the honeycomb lattice. The fractal dimension of the low angle ($<40^\circ$) and high angle ($>40^\circ$) GBs (1.52 to 1.59 and 2, respectively) is in an excellent agreement with the percolation theory predictions for finite and infinite 2D cluster fractal dimensions. As regards the fractal dimension of wetted boundaries, its non-Euclidean value (1.9 instead of 2) is likely to be distinctly visible in plotting experimental data (Fig. 4).

Oriented percolation pattern can be applied, as well as to GBW, to the solid precipitates, for example for cementite precipitates in nitrided steel (see fig. 7). Orientation anisotropy of this system illustrates a transition from 3D to 2D geometry. During nitriding of alloyed steels, the expansion of the surface layer is counteracted by the core thus leading to the appearance of biaxial compressive stresses which prohibit formation of precipitates oriented perpendicularly to the surface. Low brittleness of nitrided steels can be explained by just an increase of percolation threshold and, as a result, absence of infinite cluster of precipitates.

CONCLUSIONS

Percolation theory and inherent to it fractal geometry have been shown to be useful for analysing and predicting connectivity and topology of wetted grain boundaries ensembles at least in some systems. Further work is needed to extend the proposed approach to other materials.

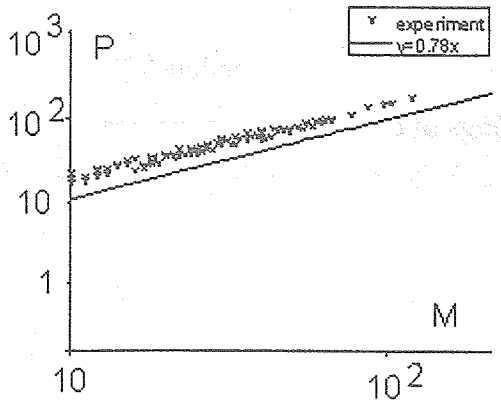


Fig.3. Fractal relation between mass and perimeter of low misorientation angle GBs clusters in Zn

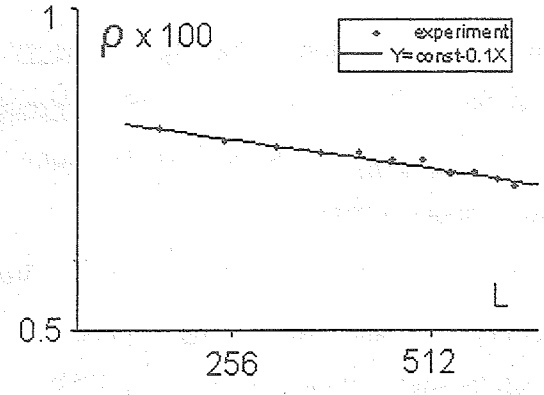


Fig.4. Fractal relation between clusters density and linear size of GBs in Zn wetted with Ga

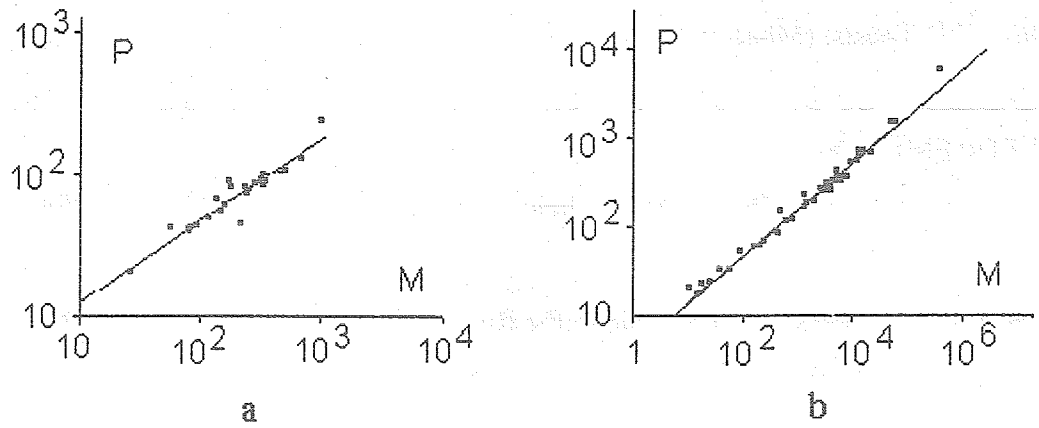


Fig.5. Fractal relation between mass and perimeter of "holes" in infinite clusters of GBs in Zn having a high misorientation angle (a) and wetted with Ga (b)

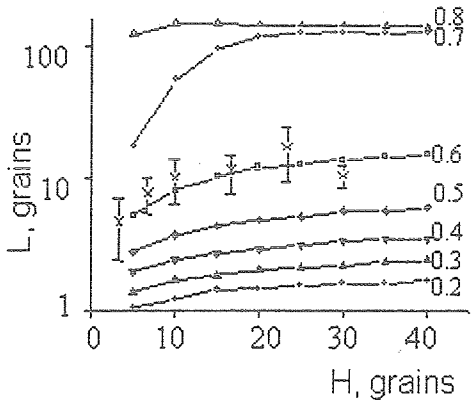


Fig.6. Penetration depth (x) of liquid Ga into 2D polycrystalline strips of Zn as compared to computer simulation for various p values

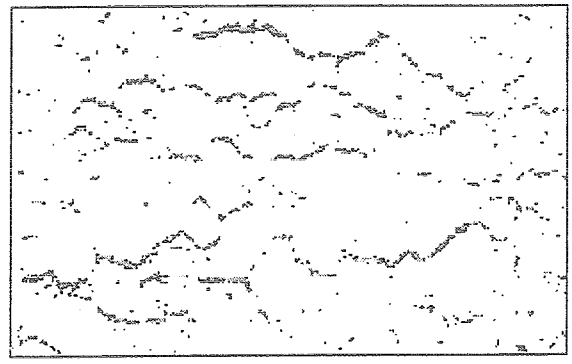


Fig.7. Cementite precipitates in nitrided layer of steel 32 CDV13

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