ROUGHNESS SCALING IN GBE MATERIALS

P.M. DUXBURY[1], E.S. McGARRITY[1] & E.A. HOLM[2]

[1] Department of Physics and Astronomy, MSU, East Lansing, Michigan 48824, USA

[2] Materials and Process Modeling, Sandia National Laboratories, Albuquerque, NM, USA

ABSTRACT

In many materials of both scientific and technological interest grain boundaries control the material properties. Important examples include structural intermetallics, high temperature superconductors and ceramic varistors. In these materials the grain boundaries can, to a first approximation, be divided into "good" boundaries with favorable properties and "bad" boundaries that degrade the material performance. Grain boundary engineering (GBE), which is also called grain boundary design, involves using sophisticated processing procedures to increase the fraction of the grain boundaries which are "good". We define the fraction of the boundaries which are "good" to be c and study the properties of model GBE systems as a function of c. The first step in this analysis is to generate realistic polycrystalline microstructures. We do this by using well established grain growth algorithms. The most important parameter in the polycrystalline microstructures we generate is the average grain size g. We then randomly choose a fraction c of the grain boundaries in the microstructure to be strong and the remainder, $1-c$, to be weak. We also define an energy ratio, ϵ, which is the ratio of the weak boundary energy to the strong boundary energy. Scaling laws for the roughness of quasistatic fracture surfaces in GBE microstructures will be compared with those which apply to diluted hypercubic lattices and with large scale simulations of realistic polycrystalline microstructures.

1. INTRODUCTION

It has been realised for some time that it is possible to improve the corrosion properties of intermetallic materials by increasing the fraction of grain boundaries which are "special" [1]. Special boundaries in this application are typically $\Sigma(3n)$ boundaries[2]. These special grain boundaries significantly enhance corrosion resistance because they are themselves resistant and also because they do not allow diffusion of the corrosive agents into the interior of the material. The corrosion susceptibility of these GBE materials is observed to decrease dramatically for $c > c_{WBP} = 0.77(1)$, which is the point at which weak boundaries cease to percolate in three dimensional polycrystalline microstructures[3]. There is a second important percolation threshold in GBE materials which occurs at the onset of an infinite cluster of strongly connected grains. The strong aggregate percolation threshold in three dimensional polycrystalline samples occurs at, $c_{SAP} = 0.12(2)$[3]. There is thus a broad regime in which a strongly connected aggegate of grains exists but at the same time a path of weak grain boundaries exists through the material. This "interpenetrating phase" regime is typical of percolating microstructures in three dimensions. In two dimensional polycrystalline systems this interpenetrating phase is absent and $c_{SAP} = c_{WBP} = 0.38(1)$[3], which is slightly higher than the bond percolation threshold for honeycomb lattices where $c_H = 0.347$.

The minimal energy surface or critical manfold (CM) is a first approximation to a quasistatic fracture surface[4] and it is also the surface on which voltage first localises in ceramic superconductors[5,6]. The CM is singular at c_{SAP} and its scaling properties have been well

studied for hypercubic lattices [7-12]. In the next section, Section 2, we summarise the scaling laws for the roughness of these interfaces both near to and away from the percolation threshold. In section 3 we show how these scaling laws can be straightforwardly extended to the study of GBE materials. In this section we test the three dimensional roughness scaling laws using large scale simulations of CM's in model polycrystalline materials. Section 4 contains some concluding remarks.

2. CRITICAL MANIFOLDS IN HYPERCUBIC LATTICES

We collect together the results found for minimum energy surfaces in bond diluted hypercubic lattices, where p is the fraction of bonds which are "strong" while a fraction $1-p$ are weak[7-12]. The energy of the strong bonds is taken to be unity while the energy of the weak bonds is ϵ, so the energy ratio is ϵ. We restrict our attention to the case of small ϵ, which is of most experimental interest.

In the two limits $p=0$ and $p=1$ the system is uniform and cleavage occurs. The energy of the minimum energy interface is $E=\epsilon L^{d-1}$ (p=0) and $E=L^{d-1}$ ($p=1$) corresponding to a cleavage plane. The roughness is zero, ie. $w=(<h^2>-<h>^2)^{1/2}=0$.

At the percolation threshold and for $\epsilon \to 0$, the manifold energy is of order one as we only need to cut one singly connected strong bond to separate the network. At p_c, we thus have, $E \approx 1$ and $w \propto L$. Using finite-size scale theory, or the nodes/links/blobs model it is easy to show that near the percolation threshold (p_c),

$$E \propto |p-p_c|^{(d-1)\nu}; \quad \text{and} \quad w \propto |p-p_c|^{-\nu} \tag{1}$$

where ν is the correlation length exponent. If the energy contrast is finite, the roughness of the interface is not as large, as an excursion of radius r from a flat interface now costs energy proportional to ϵr^{d-1}. Since there are direct paths across the infinite cluster which cut a number of strong bonds of order 1, we find a critical excursion size r_c by setting $\epsilon r_c^{d-1}=1$, which yields, $r_c \propto \epsilon^{-1/(d-1)}$. The roughness due to percolative fluctuations at p_c is thus of order r_c instead of L. The scaled roughness no longer diverges on approach to p_c, instead it reaches a plateau. The size effects due random manifold scaling ie $w \propto r_c(L/r_c)^{\zeta}$ still occur. Here ζ is the roughness exponent.

In the regime $p >> p_c$ the theory of periodic elastic media applies[13,11,12]. The key quantity in the theory is the critical length L_c which is the typical size of the cleavage regions on the critical manifold. In the limit $p \to 1$ the critical length diverges ($L_c \to \infty$) so that $w=0$. For finite $1-p$ an Imry-Ma argument provides a surprisingly good theory. In the Imry-Ma argument, we consider a fluctuation of size l from a flat surface. According to the central limit theory, the probability that such a fluctuation has energy e is given by, $P(e) \propto e^{-(e-pS)^2/[2p(1-p)S]}$, where $S=l^{d-1}$ is the number of bonds in the fluctuation and $(1-p)S/p$ is the variance in the energy of the surface. This event may occur in many places and in fact the number of places it may occur is of order L. The typical size of the largest such fluctuation is given by,

$$L^{d-1}e^{-(e-pS)^2/[2p(1-p)S]}=1 \tag{2}$$

which shows that the maximum energy gain achieved by these fluctuations is proportional to,

$$\delta e_{gain} \propto [2p(1-p)SlnL]^{1/2} \tag{3}$$

The energy cost of such a fluctuation is given by,

$$\delta e_{cost} \propto [p + (1-p)\epsilon] l^{d-2} \tag{4}$$

By comparing these two energies it is evident that at long enough length scales, the energy gain is always larger than the energy cost in both two and three dimensions. This means that on long enough length scales these manifolds are always rough. To find the "critical length" or critical sample size at which the critical manifold becomes rough, we first set $l \propto L$. Then we equate the two energies (Eq(3) and (4)) and isolate L to find that to leading order[12],

$$L_c \approx \frac{(p+(1-p)\epsilon)^2}{p(1-p)} \quad \text{and} \quad L_c \approx Exp[\frac{a_1(p+(1-p)\epsilon)^2}{p(1-p)}] \tag{5}$$

for two and three dimensions respectively. a_1 is an unknown constant. The roughness of critical manifolds then scale as, $w \propto (L/L_c)^{\zeta}$. If we consider the roughness in the limits $L \to \infty$, $\epsilon \to 0$, $p \to 1$, we find,

$$\frac{w}{L^{2/3}} \propto [(1-p)/p]^{2/3} \quad \text{and} \quad \frac{w}{L^{0.41}} \propto Exp(-ap/(1-p)) \tag{6}$$

for the two and three dimensional cases respectively. In these expressions we have used the known values of $\zeta = 2/3$ in two dimensions[7], and $\zeta = 0.41(1)$ in three dimensions[8,14]. Numerical results for the roughness as a function of p have been presented some time ago[9,10] though at that time the expressions (6) were not available. Nevertheless it is now evident that the data in refs. [9,10] are well described by the results (6).

3. CRITICAL MANIFOLDS IN GBE MATERIALS

An example of a critical manifold in a three dimensional polycrystalline microstructure is presented in Fig. 1. To obtain this figure, a three dimensional polycrystalline microstructure was grown using the Pott's model grain growth algorithm[15,16]. This algorithm provides accurate grain structures for a wide variety of polycrystalline materials. The grain growth algorithm is actually carried out on hypercubic lattices. Each site i of the lattice has an index, s_i, where this index takes one of q values ie. $s_i = 1....q$. In our simulations, we used $q = 256$ in two dimensions and $q = 100$ in three dimensions. Once we have a grain structure, we assign the bonds in the hypercubic lattice an energy based on the following rules: If two neighboring sites have the same Pott's index, then the bond is in the grain interior and the bond has unit energy. If two neighboring sites have different indices, then the bond is a grain boundary bond. At this point we have to decide which grain boundaries are "special" or "good" boundaries and which are bad. The rule we used was based on the normalized difference between the site labels of neighboring bonds $d = |s_i - s_j|/q$. We also defined the difference modulo q, so that labels $s_i = 1$ and $s_j = q$ differ by one. With this definition, grain boundaries with $d < c$ are given unit energy and those with $d \geq c$ are assigned energy ϵ. That is boundaries with small Pott's label differences are considered to be strong and those with large large Pott's label differences are considered to be weak. The procedure above leads to a polycrystalline microstructure embedded on a hypercubic lattice. The critical manifold in this microstucture (e.g. Fig. 1) is then found using the maximum flow algorithm (see e.g. [17] for a recent survey).

We have calculated many of the properties of critical manifolds in both two and three dimensional GBE materials as a function of the concentration of strong grain boundaries.

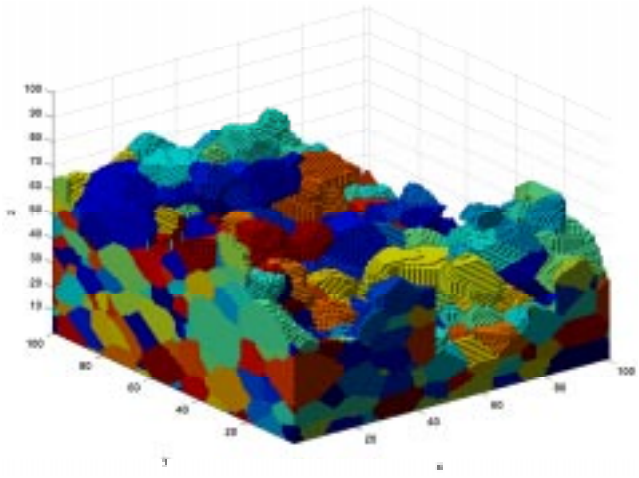

Figure 1: The critical manifold in a three dimensional polycrystalline system whose underlying cubic lattice is of size 100^3. The critical manifold shown here is for the case of a GBE material with energy contrast $\epsilon = 0.01$ with a fraction of strong boundaries $c = 0.2$.

In particular, we have calculated the energy of the manifolds, the number of bonds on the manifold, the fraction of those bonds which are weak and the roughness[3]. Here we concentrate on developing theories for roughness data as a function of c which is presented in Fig. 2. In order to understand this data, we need to generalise the analysis of the last section to the case of GBE materials. As we show below, this is quite straightforward.

We consider the limit ϵ small which is most practical interest. In that limit and for c small, the critical manifold is entirely on the grain boundaries[18]. In that case the roughness of the critical manifold is expected to scale as, $w \propto g(L/g)^{\zeta}$ This is due to the fact that the average grain size acts as an effective lattice constant, so that the effective lattice size is L/g. Near the percolation threshold we again get critical scaling, but now $\xi \propto g|c - c_{SAP}|^{-\nu}$. Similarly, $r_c \to g r_c$. Finally to find the scaling laws valid for $c >> c_{SAP}$, $\epsilon \to 0$ we write, $w = g(L/gL_c)^{\zeta}$ where L_c is given by Eqs.(5). From these expressions, we find that,

$$\frac{w}{L^{2/3}g^{1/3}} \propto [(1-c)/c]^{2/3} \quad \text{and} \quad \frac{w}{L^{0.41}g^{0.59}} \propto Exp(-ac/(1-c)) \tag{7}$$

for two and three dimensions respectively. One interesting feature of these expressions is the non-trivial scaling behavior of roughness as a function of grain size. The grain size dependence of material properties is often critical in applications due to the fact that the grain size can slowly change with time, especially in high temperature or high stress applications. The second expression in Eq. (7) is tested against numerical results in Fig. 2, which presents the data for the roughness of critical manifolds for several values of the energy contrast. The theoretical predictions are good in three dimensions (see Fig. 2) and also are surprisingly good in two dimensions (see Ref. [3]). The expressions (7) are valid for c near one. For smaller c percolative fluctuations are important and can be also be incorporated in the scaling theory in a simple way (see ref. [3]). Many other properties of experimental interest can also be related to L_c[3].

4. CONCLUSIONS

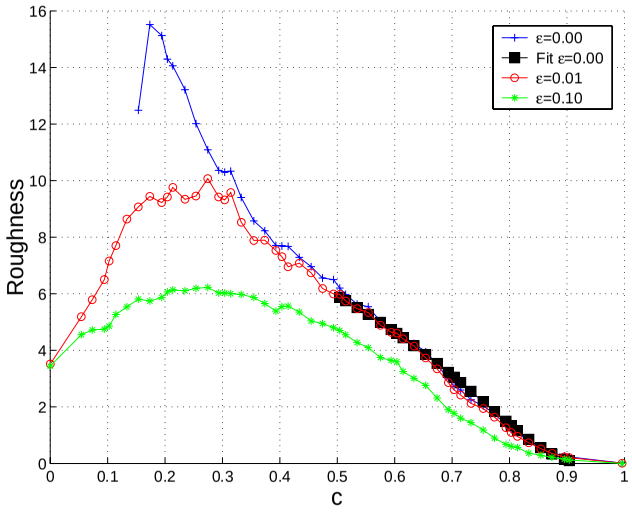

Figure 2: The roughness of critical manifolds in polycrystalline materials as a function of the concentration of strong grain boundaries (c) and for several values of ϵ. This figure is for a narrow band of values of $16 < L/g < 20$, which are quite small effective lattice sizes. Nevertheless the data is well described by the scaling law given by the second expression in Eq. (7), with $a = 0.5$ and a prefactor of 9.5 (solid circles).

We showed that the scaling theories developed to describe random manifolds in disordered hypercubic lattices can be easily extended to describe the behavior of the roughness of GBE materials. We concentrated on the limit where the energy contrast ϵ is small, which is a good approximation for many GBE materials. In that limit we defined three different scaling regimes for the critical manifold. When the concentration of strong boundaries is small ($c << c_{SAP}$) the critical manifold lies entirely on the weak grain boundaries and the scaling behavior is like that of random manifolds. In the critical regime, $c \approx c_{SAP}$, the roughness scales with the sample size, but for finite ϵ it is cutoff at a critical length $r_c = g/\epsilon^{1/(d-1)}$. In the high concentration regime $c > c_{SAP}$ the theory of periodic elastic media applies and the behavior of the roughness as a function of c is well described by Eqs. (7).

It is important to note that two dimensions and three dimensions are quite different from the point of view of grain boundary engineering. The first difference is due to the fact that in two dimensions the beginning of percolation of a strong aggregate also marks the end of percolation of weak grain boundaries, ie. $c_{SAP} = c_{WBP} = 0.38(1)$. In contrast in three dimensions there is a broad regime in which a strong aggregate percolates and paths of weak boundaries also percolate. This interpenetrating phase regime exists in the concentration range $c_{SAP} < c < c_{WBP}$ where $c_{SAP} = 0.12(2)$ and $c_{WBP} = 0.77(2)$[3]. In addition the behavior of the critical manifold as a function of c for $c > c_{SAP}$ is different in two and three dimensions due to the fact that L_c diverges algebraically as $c \to 1$ in two dimensions, while it diverges exponentially in that limit in three dimensions. This means that for a fixed concentration of strong boundaries, cleavage regions are much larger in three dimensions than in two dimensions.

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