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Calculation of the fractal dimension of grain boundaries in nanocrystalline Pd

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Abstract. The geometric structure of grain boundaries in nanocrystalline Pd has been analysed in terms of power-law relationships. The power laws yielded exponents that were interpreted as fractal-like dimensions. The box-counting fractal dimension, $\overline{d}_{2d}$, was computed for three images digitized from published transmission electron micrographs; the average result was $\overline{d}_{2d} = 1.70 \pm 0.06$. An average site occupation probability, p, was estimated for the lattices in the images, by determining the relationship between p and $\overline{d}_{2d}$ for pseudo-random fcc lattices. The results of further numerical simulations suggested that the grain boundaries had a box-counting fractal dimension of $\overline{d}_{3d} = 2.4 \pm 0.3$. The extent to which fractal theory is valid for nanocrystalline Pd is evaluated.

1. Introduction

We were recently reminded (Avnir *et al* 1998) that a physical system might be said to have a fractal structure only if it could be modelled by an intrinsically scale-free theory. This criterion is fulfilled by many grain aggregates. Cluster–cluster aggregation is essentially a scale-free process, since clusters of a range of sizes may stick together (Lin *et al* 1989). The resulting structure may be described as fractal-like if it is statistically self-similar or self-affine over a range of magnifications (Kjems 1996, p 315).

Studies using a variety of experimental methods (referred to by Lindsay *et al* 1989) have found evidence of fractal-like mass distributions in colloidal aggregates. The formative processes of such mass distributions have been modelled (Lindsay *et al* 1989) in terms of diffusion- and reaction-limited cluster–cluster aggregation. Single-particle diffusion-limited aggregation may lead to more complex, possibly self-affine, structure (Lindsay *et al* 1989).

Fractal-like mass distributions have also been observed in aggregates of evaporated ultrafine clusters. These include loose crystallites condensed at a cold finger (Siegel and Eastman 1988), crystallites lightly compacted at 100–7000 Pa (Schleicher *et al* 1995), and amorphous grains consolidated at 1.6 GPa (Sturm *et al* 1995). It is worthwhile to inquire whether fractal-like structure exists in another type of material made from aggregates of ultrafine clusters: nanocrystalline matter, made by inert-gas condensation of ultrafine grains followed by compaction.

In this paper, power laws and fractal theory are used to analyse the mass distribution in the grain boundaries of nanocrystalline Pd. The box-counting fractal dimension, $\overline{d}_{2d}$, is calculated for several transmission electron micrograph (TEM) images of thinned slices of the grain boundaries. From the value of $\overline{d}_{2d}$, the probability of site occupation, p, is estimated from numerical simulations of the grain boundaries. The value of p is used to calculate the grain

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boundaries' box-counting fractal dimension, $\overline{d}_{3d}$. The method leads to a reasonably accurate first calculation of $\overline{d}_{3d}$ for nanocrystalline Pd. The results are used to evaluate the hypothesis (Sturm *et al* 1995) that compaction can produce fractal-like structure in grain boundaries. After interpreting the data in terms of fractal theory, the validity of the interpretation is discussed with reference to the resolution range of the calculations.

2. Method

Data have been obtained from TEMs in the literature. Several TEMs of grain boundaries in nanocrystalline Pd were taken by Thomas *et al* (1989). The specimens had been made by inert-gas condensation followed by compaction in two stages (Siegel and Eastman 1988). The grains were initially consolidated into a pellet using a very low pressure, then were compacted by a pressure of approximately 1.4 GPa.

The published TEMs were digitized. Bitmaps of 602×118 (figure 1(a)), 625×118 (figure 1(b)) and 625×114 (figure 1(c)) bits were obtained. The scale of each image was approximately 1 bit $= 10^{-11}$ m. For each image, $\overline{d}_{2d}$ was calculated using a box-counting program written in *Mathematica* (Wolfram 1996). The box-counting program used the power-law *no filled boxes* $\sim$ *box length*$^{\overline{d}_{2d}}$. The relationship was approximated by varying the box length from 1 bit up to one quarter of the width of the image; this corresponded to approximately 1.5 decades (powers of 10) of resolution. The tally of filled but incomplete boxes, located at two edges of each image, was weighted by half.

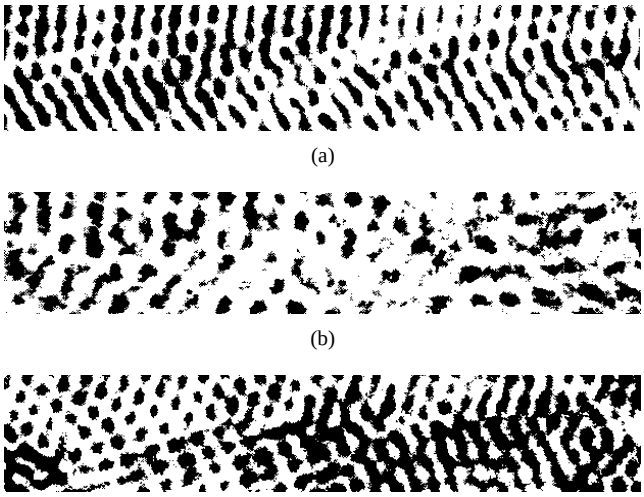
Numerical calculations were carried out to determine the approximate relationship between $\overline{d}_{2d}$ and p for the images of the grain boundaries. The calculations, made using *Mathematica* (Wolfram 1996), were performed for matrices which represented lattices that had approximately the same crystallographic structure as the images. The atomic structure of each tilt boundary was approximated as a $\{100\}$ plane in a face-centred-cubic (fcc) lattice. Pseudo-random lattices of 15×15 sites were constructed for 14 values of p in the range 0.01–1.00, then represented in close-packed form. The close-packed forms were converted to bitmap files containing 283×283 elements. By applying the box-counting program to the bitmaps that corresponded to each value of p, the value of $\overline{d}_{2d}$ was calculated as a function of p. The box length was incrementally increased from 1 to 71 bits.

Further numerical simulations were performed to determine the relationship between p and $\overline{d}_{3d}$. The effect of p on $\overline{d}_{3d}$ was determined for pseudo-random matrices generated using *Mathematica* (Wolfram 1996). The box-counting program was modified to calculate $\overline{d}_{3d}$ for three-dimensional systems. The value of $\overline{d}_{3d}$ was calculated for 14 values of p in the range 0.01–1.00. Each matrix represented an fcc lattice with $15 \times 15 \times 15$ sites, in which each site consisted of a block of $10 \times 10 \times 10$ bits. The box-counting program increased the length of boxes from 1 to 37 bits in steps of 1 bit. The value of $\overline{d}_{3d}$ was calculated from an approximation to the power-law *no filled boxes* $\sim$ *box length*$^{\overline{d}_{3d}}$. The tally of filled but incomplete boxes, at two edges of each image, was weighted by half.

3. Results

The digitized images of the grain boundaries in nanocrystalline Pd are shown in figure 1. The results of the box-counting calculations, listed in table 1, had an average value of $\overline{d}_{2d} = 1.70 \pm 0.06$. Manual box-counting yielded the value $\overline{d}_{2d} = 1.7 \pm 0.1$ for the image in figure 1(a), confirming the result that had been calculated using the box-counting program.

The box-counting results for the simulated lattices (figure 2) showed that $\overline{d}_{2d}$ increases



(a)

(b)

(c)

Figure 1. Grain boundaries in nanocrystalline Pd. The images were digitized from TEMs in the literature (Thomas *et al* 1989) and have been clipped to the same size. The (a), (b) and (c) TEMs had different magnifications. Black (atoms) and white are reversed, compared to the originals.

Table 1. Computed box-counting fractal dimensions of the named images.

Figure	$\overline{d}_{2d}$
1(a)	1.70 ± 0.04
1(b)	1.60 ± 0.11
1(c)	1.79 ± 0.03

with increasing p. The data was fitted by an equation of approximately $\overline{d}_{2d} = 1.9 + 0.20 \ln p$. The calculated value of $\overline{d}_{2d}$ was not equal to 2 at $p = 1$. When the box length became large, the number of filled boxes remained constant over small ranges of box lengths, altering the gradient of the fitted line despite the maximum box length being set to a relatively small fraction of the image width. The fitted equation deviates from the data in the range of $p = 0.2$–0.3, but appears to be reasonably accurate near the box-counting result of $\overline{d}_{2d} = 1.70 \pm 0.06$. Using the fitted equation for $\overline{d}_{2d}$, it was found that the grain boundaries in figure 1 had an average site occupation probability of $p = 0.4 \pm 0.1$.

When the box-counting program was applied to the simulated fcc lattices, it was found that $\overline{d}_{3d}$ increased with increasing p. The relationship between the two quantities was approximately $\overline{d}_{3d} = 2.7 + 0.29 \ln p$ (figure 2). At $p = 0.4 \pm 0.1$, which was the average value for the images in figure 1, the corresponding value of $\overline{d}_{3d}$ was 2.4 ± 0.1. However, the result was made more uncertain by the effect of large box lengths on the data and gradient, demonstrated by the fact that $\overline{d}_{3d}$ was not equal to 3 at $p = 1$. The final result was $\overline{d}_{3d} = 2.4 \pm 0.3$.

4. Discussion

It is reasonable to consider the possibility that $\overline{d}_{2d}$ and $\overline{d}_{3d}$ had non-integer values due to the presence of fractal structure. Fractal structures can be formed by the same processes which were involved in the synthesis of the nanocrystalline specimens: condensation (Siegel and Eastman 1988), light compaction (Schleicher *et al* 1995) and heavy compaction

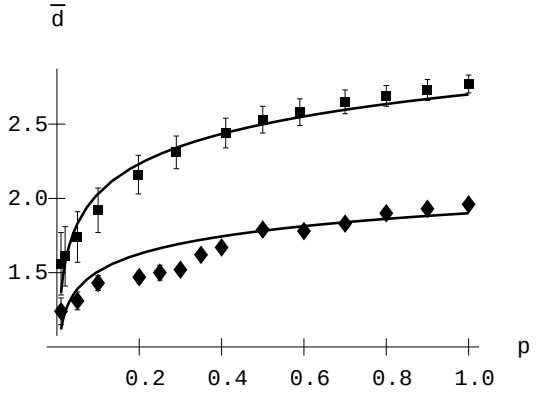


Figure 2. Relationship between p and the scaling exponent of the mass distribution on an fcc lattice. Diamonds: $\overline{d}_{2d}$ versus p. Squares: $\overline{d}_{3d}$ versus p. The solid curves are the fitted curves, described by the equations given in the text.

(Sturm *et al* 1995). Furthermore, the formation of the grain boundaries may have involved some cluster–cluster aggregation, which is a scale-free phenomenon.

Before fractal theory is invoked, however, the mass distribution must be shown to behave according to a power-law over a range of resolutions. A power-law analysis of the images in figure 1 was justified by the low uncertainties in the calculated values of $\overline{d}_{2d}$ (table 1). Although the measured range of resolutions was rather small, it is acceptable within the current usage of fractal terminology. Recently, Avnir *et al* (1998) reviewed a selection of studies in which fractal theory had been applied to physical systems. The scaling ranges were typically between 0.5 and 2.0 decades, and had a median value of 1.3 decades. For example, in a previous study of fractal structures in Pd (Schleicher *et al* 1995), the measurement range spanned approximately one half of a decade. Biham *et al* (1998) have observed that such limited-range fractal structures are abundant in nature. However, the actual range of the self-similarity in nanocrystalline Pd may be greater than the measured range. This could be tested in future work by comparing the fractal-like dimension of the grain boundaries to that of the entire compacted aggregate.

The observation that fractal structure can exist after compaction is consistent with the results of previous studies. Even though the grains may slide and become rearranged during compaction (Sturm *et al* 1995), the rearrangements may be relatively small. For example, aggregates of ultrafine Pd grains have fractal-like structures after light compaction in pressures of 100–7000 Pa (Schliecher *et al* 1995). The scaling exponent of the radial mass distribution, D_f, was calculated to be 2.54–2.75 from the particles' mobility and inertia (Schliecher *et al* 1995). The range of values of D_f lies within the uncertainty range of 2.1–2.7 which was calculated in the present study. The similarity between the values of $\overline{d}_{3d}$ and D_f suggests that fractal-like structures can form over a range of compaction pressures, and that the fractal dimension might not be greatly affected by the compaction pressure.

5. Conclusions

The mass distribution in nanocrystalline Pd grain boundaries is non-Euclidean and has fractal-like characteristics. The interpretation of the scaling exponent as a fractal-like dimension is justified by the similarity between its value and those of agglomerates with fractal structures, and by the fact that the grain boundaries' formation process probably involved

some cluster–cluster aggregation. Thinned slices of the grain boundaries, prepared for TEM experiments, have a box-counting dimension of approximately $\overline{d}_{3d} = 2.4 \pm 0.3$, while their images have a box-counting dimension of $\overline{d}_{2d} = 1.70 \pm 0.06$.

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