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Quantitative analysis of the microstructural homogeneity of zirconia-toughened alumina composites

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Abstract

The Voronoi diagram approach was applied to quantify the level of microstructural homogeneity of ceramic ZTA samples. From SEM pictures of polished cross-sections of ZTA samples a point pattern representing the distribution of the zirconia phase in the composite was generated. This point pattern was converted into a Voronoi diagram. The level of microstructural homogeneity was quantified by statistical analysis of the relevant properties (area, perimeter and number of faces) of the Voronoi polygons. A dimensionless parameter defining the level of microstructural homogeneity was calculated from the different sets of statistical data. The calculated parameters indicated significant differences in homogeneity between the ZTA samples. These differences were in qualitative agreement with previously published wear rates of the same ZTA composites. This illustrates the relevance of microstructural homogeneity for wear performance. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Many properties of ceramics are related to their microstructure. Inhomogeneities in the local morphology can have a large effect on properties like strength, wear

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resistance and fatigue. A quantitative measure for the homogeneity of a microstructure is required in order to be able to characterize the final microstructure unambiguously.

Visual inspection of SEM pictures is most commonly used in literature to get an impression of the microstructural homogeneity [1–4]. Placing a grid over the image and counting the grains of one phase within each cell [5] or the mean intercept length [6] of the grains provides a more quantitative measure of the homogeneity. However, in the latter case the result is very sensitive to the size of the grid.

An alternative approach was followed by Samardzija et al. [7], who simulated three types of point patterns, i.e. clustered patterns, random patterns and ordered patterns. Statistical data gathered from the simulated patterns were compared with the statistical data obtained from patterns representing the zirconia phase distribution in real zirconia-toughened alumina (ZTA) composites. This gave a semi-quantitative measure for the level of homogeneity of the ZrO_2 phase distribution in the Al_2O_3 matrix.

In the present study, a method for full quantification of the microstructural homogeneity of two-phase composites is proposed and applied to a number of ceramic samples. For the analysis of microstructures SEM pictures are made of 2D sectionings of polished and etched samples. With an image analysis program the centers of cross-sections of the grains of the dispersed phase are determined. The distribution of these centers is converted into a Voronoi diagram, which gives a schematic representation of the microstructure. In short, each cell of the Voronoi diagram represents the center of a particle or region of the dispersed phase in the surrounding matrix phase. The cells have easily quantifiable properties like surface area, perimeter length and an integer number of faces. A measure for the homogeneity of the compact is derived from the statistical variance in these data.

The analysis method is applied here to three ZTA samples, which differ with respect to the conditions used during their colloidal processing. The tribological properties of these composites were already reported by Kerkwijk and co-workers [1,2]. They suggested that ZTA composites with a homogeneous microstructure have superior wear resistance. In the present study the same samples were examined and their degree of microstructural homogeneity was determined quantitatively. The results are compared with the tribology data of Kerkwijk and co-workers [1,2].

2. Theory

The principle of constructing a Voronoi diagram from a distribution of points $\{p_1, \ldots, p_N\}$ is as follows: space is divided into cells, each consisting of the positions closer to one particular point p_i than to any other. Every location in the plane is thus assigned to the closest member of the point set $\overline{p}$ and every member of this set forms its own region with locations assigned to it. Each location is assigned to at least one member. The locations that are assigned to two or more members form the boundaries of the regions. The tessellation thus obtained is referred to as a Voronoi diagram and the regions are called Voronoi polygons [8]. In the present analysis of ceramic microstructures, the points p_i represent the center of mass of the ZrO_2 phase dispersed in the ZTA samples. An advantage of using a Voronoi diagram instead of the center of mass is that the former contains a direct measure to the average number of neighboring grains or phases. Voronoi tessellation [9] is also known as Dirichlet [10], Thiessen or Ziegler–Natta tessellation.

The convex hull of a Voronoi diagram is the collection of outer boundaries of all closed Voronoi polygons. Polygons on the outside of the convex hull, i.e. in contact with the edge of a SEM picture, are excluded from the analysis. The relevant properties of a Voronoi polygon are its area, perimeter and number of faces. A dimensionless number HP_q, expressing the level of homogeneity, can be defined by taking the standard deviation σ_q of the respective property q, normalized with respect to its average value μ_q:

$$HP_q = \frac{\sigma_q}{\mu_q}, \tag{1}$$

with

$$\mu_q = \frac{1}{N}\sum_{i=1}^{N} q_i, \tag{2}$$

$$\sigma_q = \sqrt{\frac{\sum_{i=1}^{N}(q_i - \mu_q)^2}{N-1}}. \tag{3}$$

The property q indicates area size (A), perimeter (l) or number of faces (n) of a polygon. A small value of HP_q indicates a homogeneous microstructure.

It should be noted that an ideally homogeneous 3D microstructure will exhibit HP parameters larger than zero when only 2D cross-sections of the 3D structure are considered in the analysis. An example of such a microstructure is the 3D random distribution of monodisperse spherical particles of diameter d_V. This hypothetical system is a representative case of an ''ideal'' ceramic microstructure. However, a cross-section of this microstructure will show a distribution of circles with different diameters z ($0 < z < d_V$). The distribution function of the diameters apparent in the cross-section is $f(z) = z/(d_V\sqrt{d_V^2 - z^2})$ [11]. Using the continuous definitions for the average and standard deviation, i.e. $\sigma_q^2 = \int_0^{d_V}(q(z) - \mu_q)^2 f(z)\,dz$ and $\mu_q = \int_0^{d_V} q(z)f(z)\,dz$, and replacing $q(z)$ by the expressions for the surface area $(q(z) = (1/4)\pi z^2)$ or perimeter of a circle $(q(z) = \pi z)$, it can be shown easily that $HP_A = (1/5)\sqrt{5} \approx 0.45$ and $HP_l = \sqrt{96 - 9\pi^2}/3\pi \approx 0.28$. These values thus represent theoretical lower limits.

In theory there are no upper limits to the values of the HP parameters.

3. Experimental

Undoped zirconia suspensions were made by precipitation of diluted $ZrCl_4$ (Merck, Darmstadt, Germany) solutions in an excess of ammonia. After washing with water

Table 1
Compositions of the suspensions used for colloidal processing of ZTA compacts, and the green densities before and after sintering

Composite	HNO_3 (mol/l)	Al_2O_3 (wt.%)	ZrO_2 (wt.%)	ρ_{green} (%)	$\rho_{sintered}$ (%)
A	0.05	50	33	54	>99
B	0.05	66	33	57	>99
C	0.10	50	33	59	98

and ethanol and drying, the zirconium hydroxide precipitate was calcined at 500°C for 2 h. The resulting zirconia powder was suspended using HNO_3 as the stabilizing agent [1,2,12]. Single-phase alumina suspensions were made from commercially available alumina powder (AKP-50, Sumitomo Chemical Co. Ltd., Osaka, Japan) using the stabilizing agent. The powder loadings of the single-phase suspensions are listed in Table 1. The suspensions were then ball-milled separately, after which they were mixed in the appropriate mass ratio for the composite (85 wt.% Al_2O_3; 15 wt.% ZrO_2), and filtered. The green compacts were released from the membrane filter after drying at room temperature. They were sintered for 2 h at 1450°C (heating and cooling rates of 2 and 4°C/min, respectively). This resulted in samples of 97–99% density, and with an average grain size of 0.7 μm for alumina and 0.3 μm for zirconia. Following the notation used in Table 1 the samples are denoted as composite A, B, or C. For further details the reader is referred to [1,2].

SEM pictures with identical size, resolution (number of pixels) and scale were taken from the polished and thermally etched samples. They were analyzed using the Image Pro Plus 3.0 software package (MediaCybernetics, Silver Spring, MD). The spatial distribution of the zirconia phase was determined by converting the original image into a binary black/white image. Hence the shape and size of the grains is not explicitly made use of. The black/white threshold value used in binarization was set such that the black/white ratio in the picture is equal to the volume ratio of the alumina and zirconia present in the sample. The center of mass of the dispersed zirconia phase were determined from the binary images. A home-made software code was used to construct Voronoi diagrams from these center of mass. The program calculates the area, perimeter and number of faces of each Voronoi polygon, and the respective averages and standard deviations for the set of polygons inside the convex hull. From the latter data the homogeneity parameters HP were calculated.

4. Results and discussion

Fig. 1 shows the microstructures of the composites used in this study. The white and gray grains consist of ZrO_2 and Al_2O_3, respectively. The same images after binarization are shown in Fig. 2. The corresponding Voronoi diagrams constructed from these binary images are shown in Fig. 3. In Table 2, the homogeneity parameters calculated for the area HP_A, perimeter length HP_l and number of faces HP_n are listed.

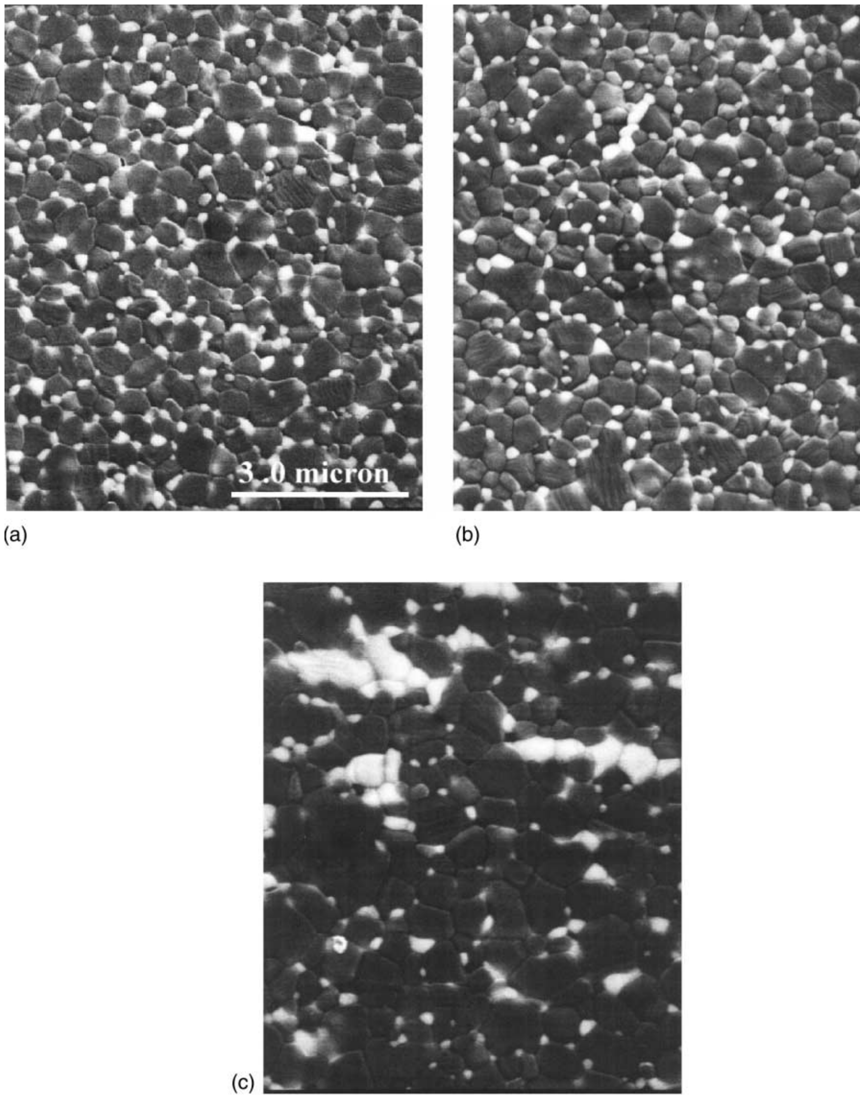


Fig. 1. SEM pictures showing the microstructure of (a) composite A, (b) composite B, (c) composite C.

Clearly the HP values determined from the area and perimeter distributions are largest for composite C, which indicates that the ZrO_2 phase is dispersed less homogeneously than in composites A and B. Comparison of the HP_n parameters for the number of faces is less conclusive. This is mainly due to the discrete nature of this property, and the fact that for the majority of 2D polygons the number of faces falls in the range of 5–7. The HP_n parameter is therefore less sensitive to variations in the microstructural homogeneity than the area size and perimeter distributions.

The calculations were repeated on fragments of the original images (70% of the original area). For composites A and B this resulted in similar values as in

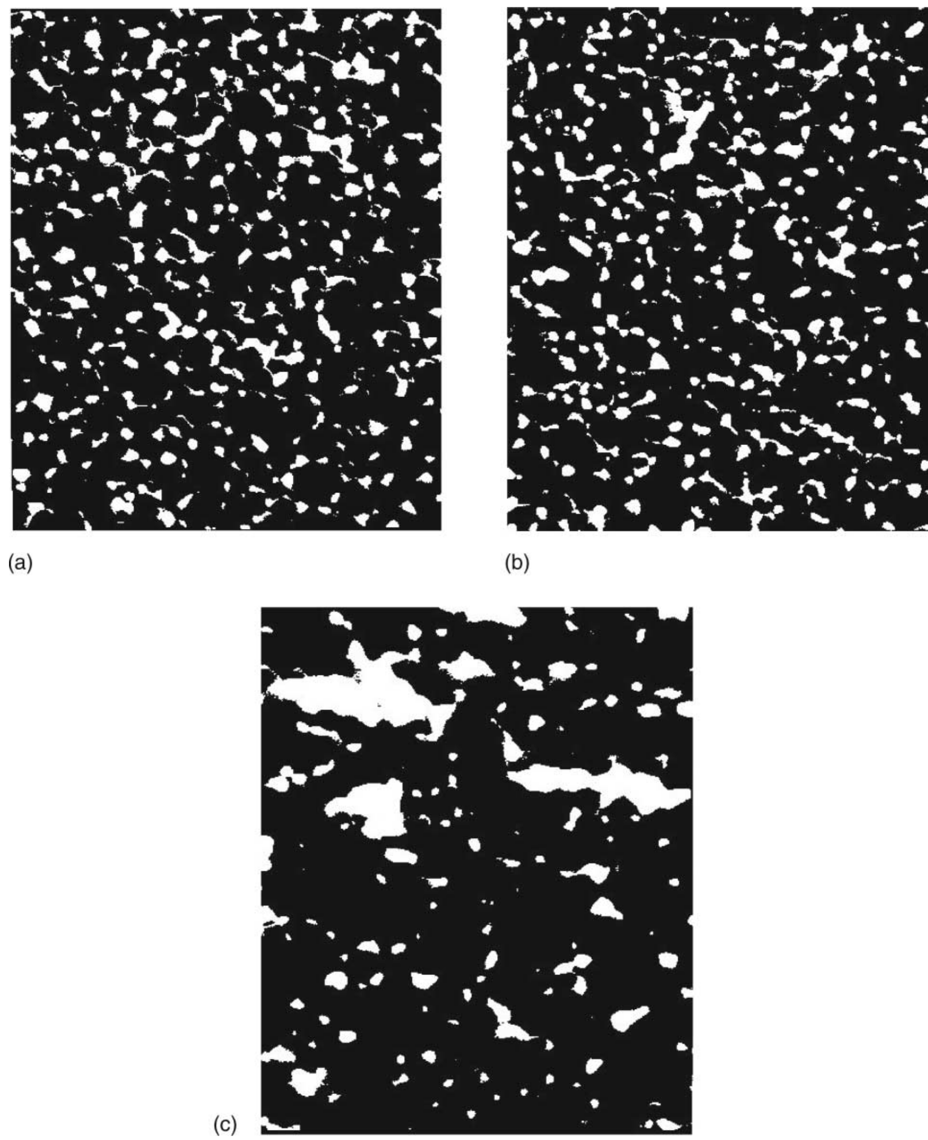
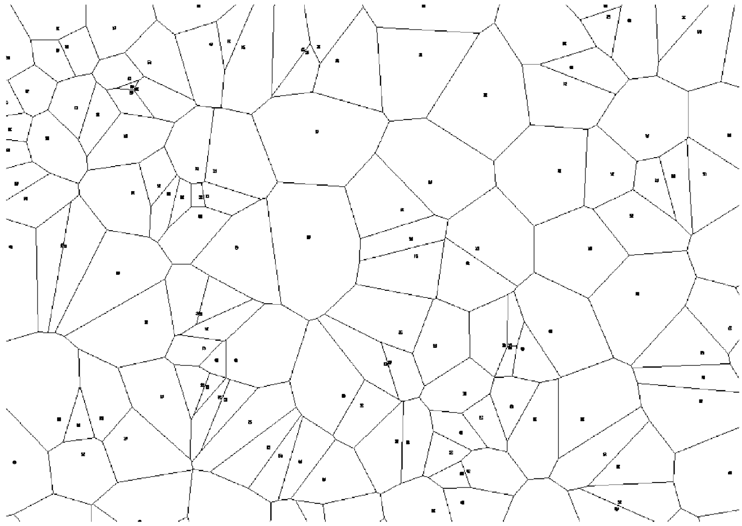


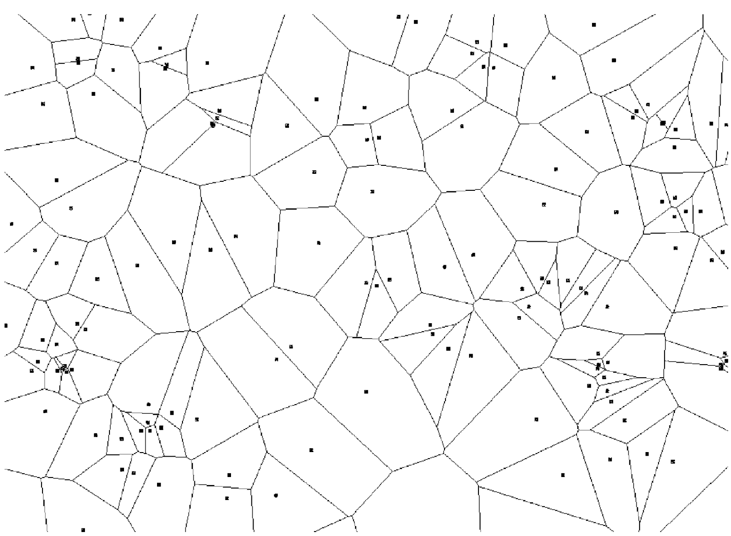
Fig. 2. The corresponding binary images of Fig. 1a–c with set black/white ratios corresponding the volume ratio of the dispersed Al_2O_3 and ZrO_2 phases in the ZTA composites.

Table 2, while for composite C the HP values depended much more strongly on the actual choice of the fragment. This indicates that composite C has a relatively low level of homogeneity on the scale of the picture, while composites A and B appear homogeneous.

Table 3 lists the specific wear rates of samples A–C. Kerkwijk et al. measured a specific wear rate $k_w = 5 \times 10^{-8}$ mm^3/N m for composite B and comparable behavior for composite A, but a very low wear resistance for composite C [1]. They



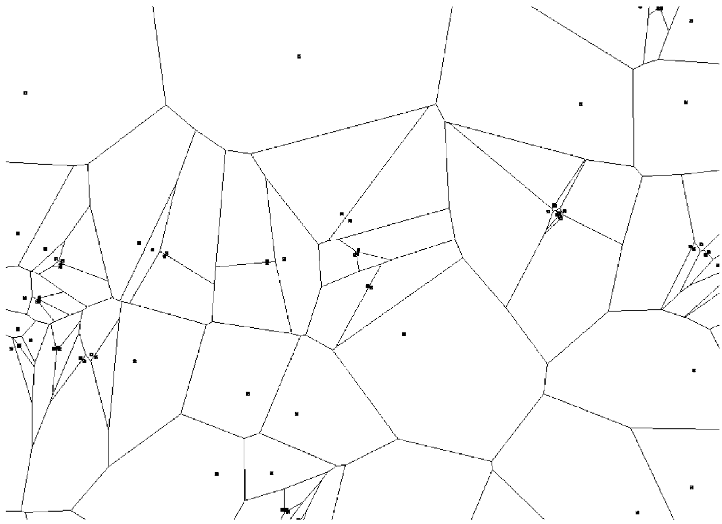
(a)



(b)

Fig. 3. Voronoi diagrams representing the ZrO_2 phase distribution in (a) composite A, (b) composite B, (c) composite C.

explained these results by assuming the microstructural homogeneity of composites A and B to be superior. The poor performance of composite C is caused by the high concentration of HNO_3 used in its preparation, which causes agglomeration of ZrO_2. The present analysis, in which the microstructural homogeneity of these composites is quantified, confirms this explanation.



(c)

Fig. 3. (*Continued*).

Table 2
Homogeneity parameters HP calculated from the area (*A*), perimeter (*l*) and number of faces (*n*) distributions, respectively[a]

Composite	HP_A	HP_A/HP_{ideal}	HP_l	HP_l/HP_{ideal}	HP_n
A	0.69	1.54	0.35	1.23	0.25
B	0.70	1.57	0.34	1.20	0.26
C	0.93	2.08	0.52	1.83	0.28
Ideal microstructure	0.447	1	0.284	1	–

[a] Calculated HP values for an ideal microstructure (a 3D random distribution of monodisperse spherical particles) are shown for comparison.

Table 3
The specific wear rates of samples A–C as reported in [1]

Composite	Specific wear rate k_w (mm^3/N m)
A	$\sim$1–10 $\times 10^{-8}$
B	5 $\times 10^{-8}$
C	$>10^{-6}$

5. Conclusions

The distribution of the ZrO_2 phase in dual-phase ZTA composite microstructures can be represented by Voronoi diagrams that are constructed from binary images derived from cross-section images of the ceramic microstructures. To represent the level of microstructural homogeneity of a microstructure quantitatively a dimensionless homogeneity parameter HP was defined, based on the distributions of area, perimeter or number of faces of the polygons in the convex hull of the Voronoi diagram. As reference values the HP_A and HP_l parameters of a hypothetical ideally homogeneous microstructure were calculated. These values indicate theoretical lower limits.

The method was tested on three ZTA composites with known tribological properties. The quantitative analysis indicated differences between the levels of homogeneity in different bodies. The differences were in qualitative agreement with the assumption made in literature [1] that the specific wear rate of a ceramic body decreases with decreasing level of microstructural homogeneity. The HP values that are based on the area or perimeter distributions appear to be most sensitive to differences in microstructure.

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