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Numerical calculations of the thermal conductivity of porous ceramics based on micrographs

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Abstract

The overall thermal conductivity of a porous material is strongly sensitive to the volume fraction and spatial distribution of the pores. For this second aspect analytical models predicting thermal conductivity as a function of pore volume fraction are obliged to make a simplifying assumption concerning the pore shape. In order to describe the effects of the microstructure on heat transfer in greater detail, we have developed a method involving 2D finite element calculations based on real micrographs of the porous solid. The approach was tested on micrographs of tin oxide samples with pore contents from 10% to 50%. Quantitative results obtained for pore contents up to 20% give very good agreement to Rayleigh's model. Higher pore contents lead to a number of difficulties but the qualitative results are used to support the choice of Landauer's effective medium expression as an appropriate general analytical model for the thermal conductivity of a porous ceramic material.
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Keywords: Thermal conductivity; Porosity; Finite element methods

1. Introduction

Knowledge of the mechanical and thermal properties of materials is essential for industry, guiding material choice for specific functions. In this work we focus on heterogeneous ceramics. Economically important examples are refractories, cements, and clay based products which, though low cost, are made in very large quantities. Such materials exhibit complex microstructures consisting of a mixture of different solid phases in granular form, interfaces, eventually cracks, and pores. As part of a long term systematic study of these factors with respect to heat transfer through a solid, the present paper examines the influence of porosity on the overall thermal conductivity of a ceramic material.

In essence this can be considered as a two-phase mixture problem where the solid phase and the pore phase are each characterised by constant, but strongly different, values of thermal conductivity. The presence of interfaces in a polycrystalline ceramic material can be taken into account by a small modification to the solid phase thermal conductivity.[1] There are a significant number of analytical expressions which then describe the effect of pore volume fraction as a variable on the thermal conductivity of a porous solid.[2–5] In each case, the expression is based on a geometrical simplification of the microstructure concerning the spatial distribution of the pore phase in the solid matrix. For example, Rayleigh's expression treats the pore as an obstructing cylinder to the heat flow.[6] The Maxwell–Eucken expression describes the heat flow around a spherical inclusion,[7] corresponding well to the physical reality of a small volume fraction of dispersed closed pores in a solid medium. These approaches become limited when the pore volume fraction increases and the shape of the pore becomes tortuous; or in other words the isolated equiaxed pores now become connected. Landauer's expression for effective medium percolation theory (EMPT) is interesting because the connectivity of the phases is taken into account[8,9] and this has been used to describe open porosity in alumina up to volume fractions of 40%.[1] The development and increased capacity of computers with their associated software packages over the last 30 years open up an alternative approach. Finite element analysis

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software can now calculate mechanical stress/strain fields or temperature/heat flow distributions for rather complex three-dimensional objects in steady state or dynamic conditions. We have therefore attempted to apply the finite element approach to porous microstructures in order to obtain the most faithful possible representation of our materials. The important advantage should be to handle the aspect of phase connectivity in a more satisfying manner. The starting point is a micrograph of a given sample. After treatment to obtain a binary image, an automatic process is used to generate a two-dimensional mesh representing the sample. A two-dimensional computer calculation of the heat flow resulting from a temperature difference across the mesh is then performed allowing the thermal conductivity to be evaluated. The present paper describes numerical simulations that have been made on micrographs corresponding to tin oxide samples with pore volume fractions from 10% to 50%. Results are compared to predictions made by the analytical expressions of Rayleigh and Maxwell–Eucken as well as EMPT. Prior to that, the approach was tested on objects with simple geometries; that is an isolated sphere in a cube and an isolated cylinder in a cube, in order to assess the accuracy of the procedure.

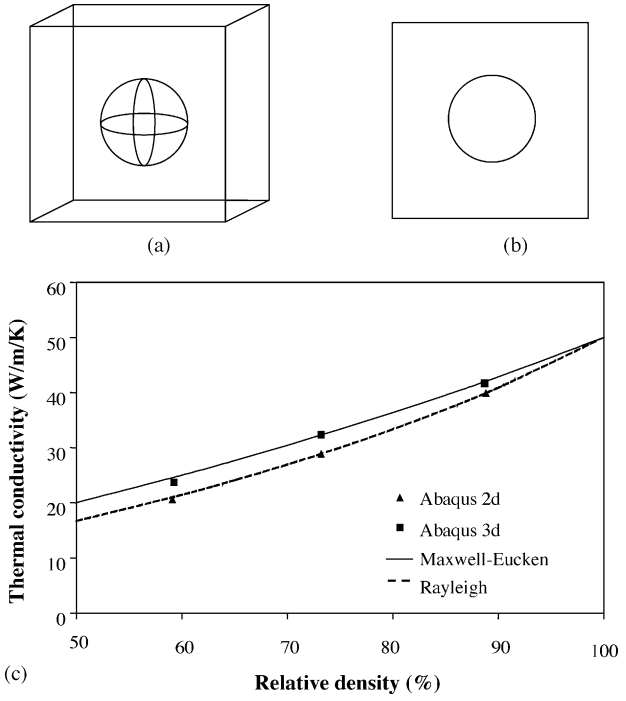


Fig. 2. Simple geometries used to test numerical simulation procedure in comparison to the Maxwell–Eucken and Rayleigh expressions. (a) 3D structure: spherical inclusion in a cubic matrix, (b) 2D structure: disc centred in a square matrix, (c) calculated values of thermal conductivity as a function of relative density.

2. Experimental procedure

2.1. Samples

Samples in the form of discs, 8 mm in diameter and 2 mm in thickness were made using a standard ceramic processing route. This consists of uniaxially pressing a dry powder in a die followed by sintering of the green pellet in an electrical furnace. For the tin oxide samples a sintering additive was necessary. MnO_2 (Aldrich) was therefore added to 99.9% pure SnO_2 powder (Aldrich) in an amount of 0.5 wt%. The powder was attrition milled for 1 h in ethanol. After removal of the ethanol by evaporation (12 h at 60 °C), the powder was thermally treated at 400 °C for 4 h.[10] The pressed discs were sintered between 1000 °C and 1150 °C to yield relative densities from 50% to 90%.

2.2. Characterisation

Sample densities were evaluated using the method based on Archimedes' principle.

2.3. Numerical simulation

2.3.1. Acquisition of images and treatment

The microstructures were examined by scanning electron microscopy. Given that the typical grain and pore sizes are situated around the micron or smaller, the dimensions of the region under study were chosen in the range 5 μm × 5 μm to 10 μm × 10 μm. A micrograph is then taken for treatment by

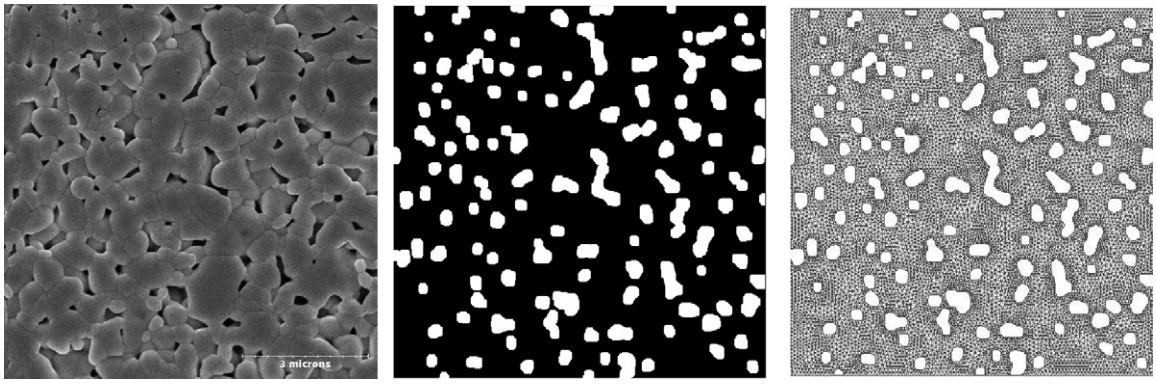


Fig. 1. Micrograph, binary image and mesh used in numerical simulation procedure.

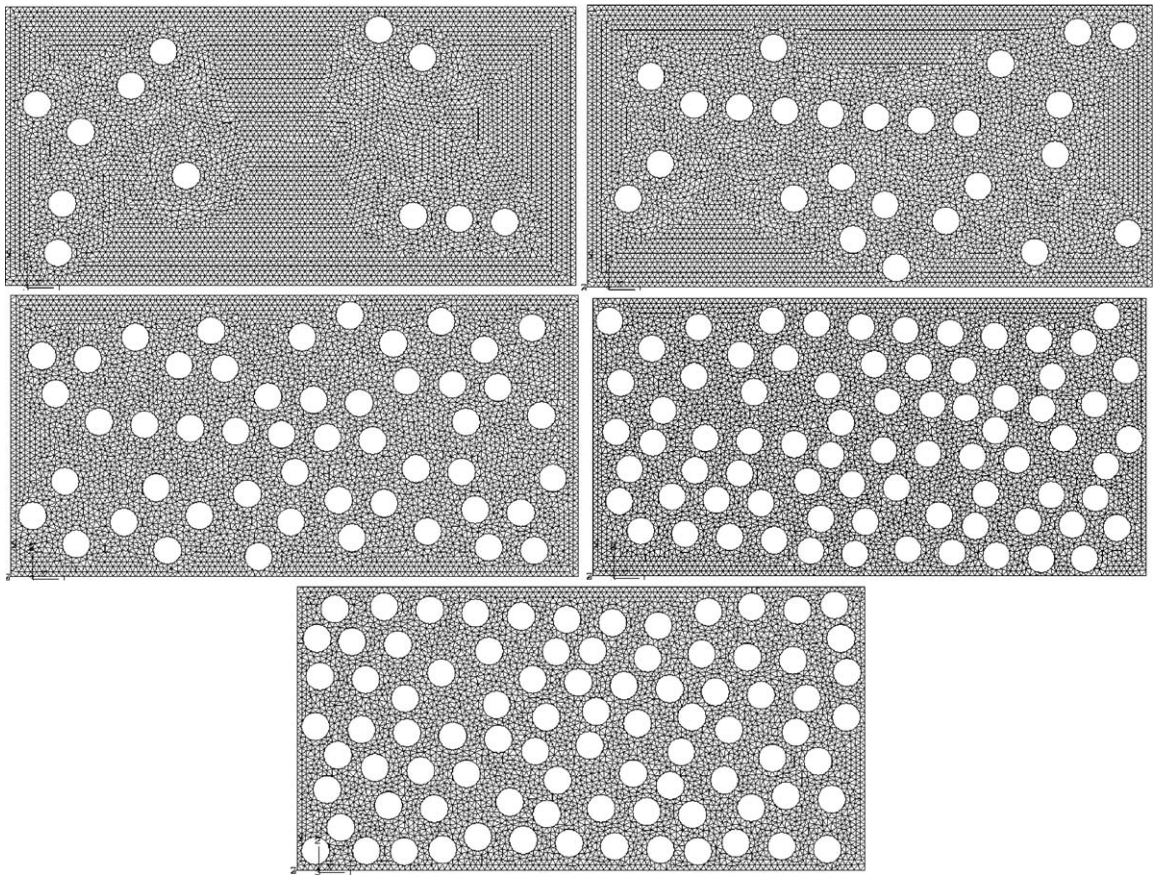


Fig. 3. Representative examples of random distributions of discs for each pore volume fraction studied.

image analysis software (Aphelion). In this step the image is simplified into two levels of grey: the black represents the solid phase, the white, the porous phase (Fig. 1). A fine adjustment of the threshold grey level value between the solid and pore phases is used to make the white phase fraction equal to the measured pore volume fraction of the real sample. A meshing of the black phase then gives a file used for numerical simulation.

2.3.2. Simulations

Simulations were made using a numerical technique based on finite element analysis. A software package called "Abaqus" was used. A temperature difference ΔT was imposed across the upper and lower boundaries of the geometrical model obtained from treatment of the micrograph. These boundaries are parallel and separated by a distance e. The white phase representing the pore is assigned with a thermal conductivity value of zero. Heat simply flows through the black (solid) phase. We then calculate the thermal conductivity of the structure from the average heat flow per unit area ϕ found at the lower boundary of the 2D image. The conductivity is given by the expression:

$$\lambda = \frac{\phi e}{\Delta T} \quad (1)$$

3. Results and discussion

Before making calculations based on micrographs of real materials, the accuracy of the procedure was studied on the simpler geometry of a single pore inclusion in a solid cubic matrix. In particular geometries corresponding to the well known expressions of Maxwell–Eucken[7] and Rayleigh[6] were chosen (Fig. 2). Thus the numerical values could be compared

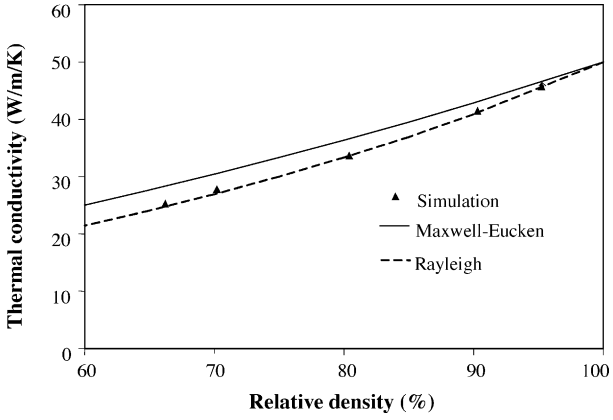
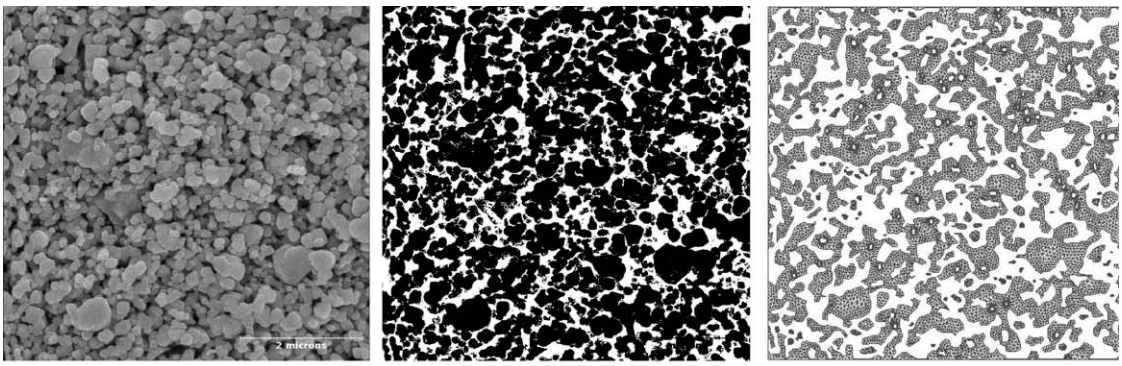
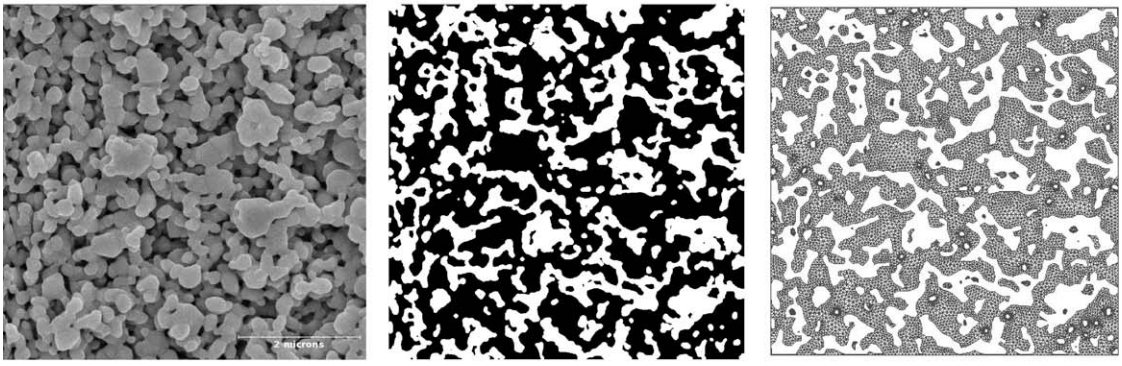


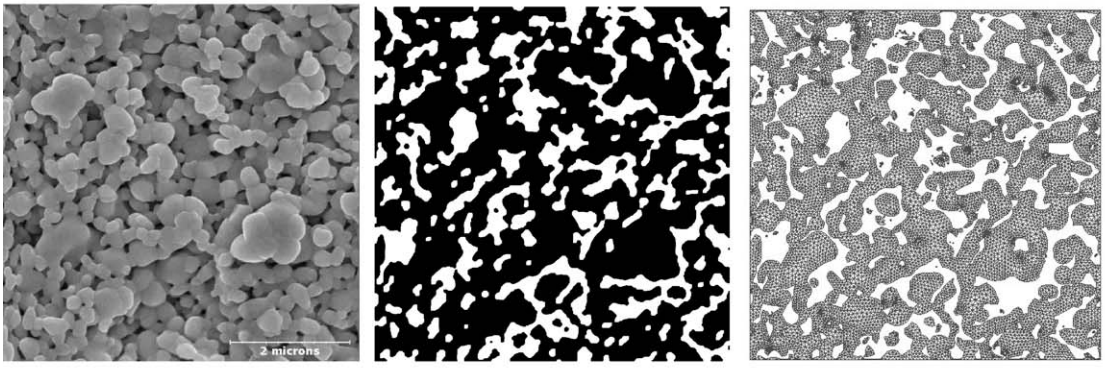
Fig. 4. Comparison of values of thermal conductivity as a function of relative density between the numerical simulations using random distributions of discs and the analytical models.



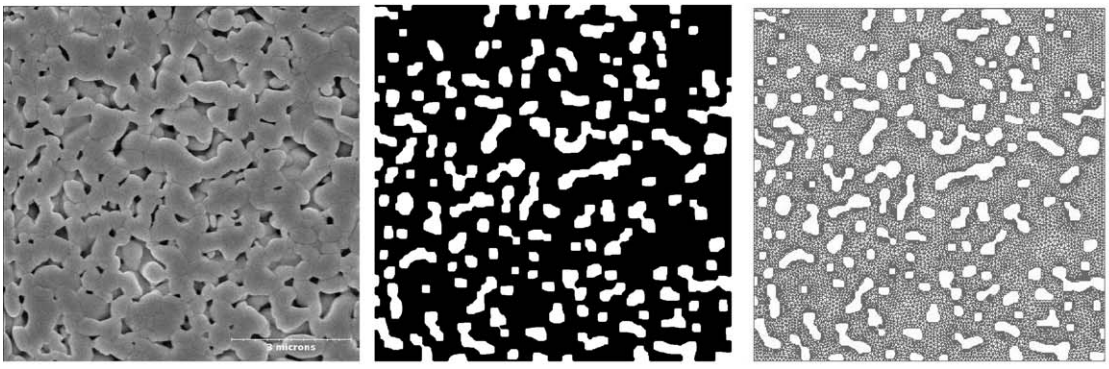
(a) **sample with 50% of pore volume fraction**



(b) **Sample with 40% of pore volume fraction**

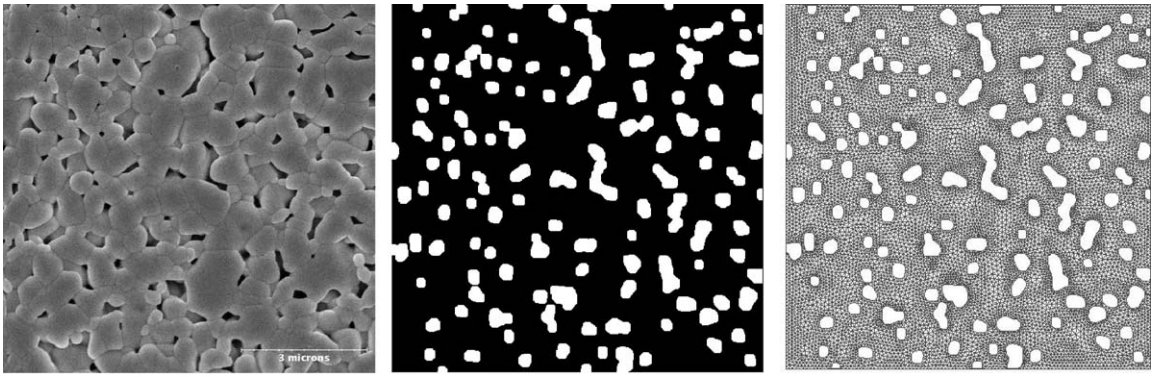


(c) **Sample with 32% of pore volume fraction**

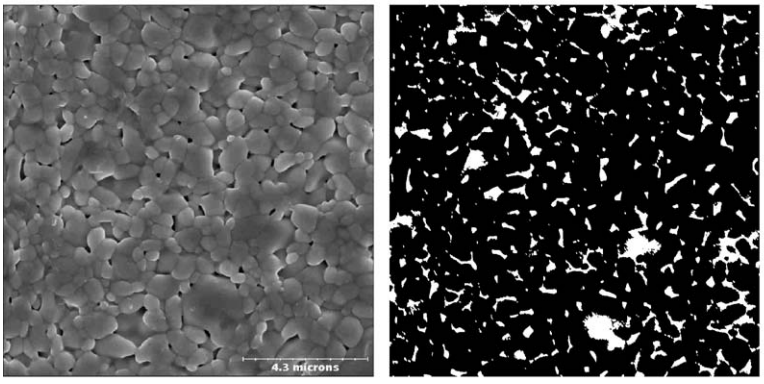


(d) **Sample with 25% of pore volume fraction**

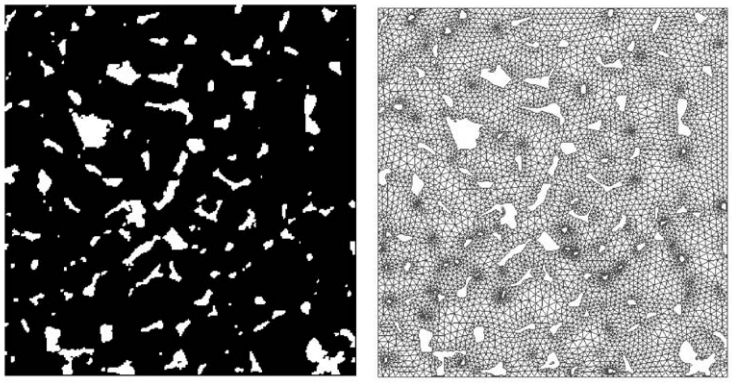
Fig. 5. Micrographs, binary images and meshed structures for samples of different relative density. (a) Sample with 50% of pore volume fraction, (b) sample with 40% of pore volume fraction, (c) sample with 32% of pore volume fraction, (d) sample with 25% of pore volume fraction, (e) sample with 18% of pore volume fraction, (f) sample with 11% of pore volume fraction, (g) magnified image for the sample with 11% of pore volume fraction.



(e) **Sample with 18% of pore volume fraction**



(f) **Sample with 11% of pore volume fraction**



(g) **Magnified image for the sample with 11% of pore volume fraction**

Fig. 5. (*Continued*).

directly to those predicted by the analytical expressions as a function of pore volume fraction. The approach was then generalised by numerical simulation of the thermal conductivity for a random distribution of identically sized inclusions in the matrix.

3.1. Simple geometries

The Maxwell–Eucken expression predicts the overall thermal conductivity λ_a of a spherical inclusion, centred in a solid cube of conductivity λ_m and is given by:

$$\lambda_a = \lambda_m \left[\frac{\lambda_p + 2\lambda_m + 2v_p(\lambda_p - \lambda_m)}{\lambda_p + 2\lambda_m - v_p(\lambda_p - \lambda_m)} \right] \quad (2)$$

where the inclusion has thermal conductivity λ_p and relative volume v_p.

The Rayleigh expression corresponds to the two-dimensional situation of a disc in a square matrix and is given by:

$$\lambda_a = \lambda_m \left[\frac{\lambda_p + \lambda_m + v_p(\lambda_p - \lambda_m)}{\lambda_p + \lambda_m - v_p(\lambda_p - \lambda_m)} \right] \quad (3)$$

where the symbols have the same meaning.

In fact this two-dimensional structure is equivalent in three dimensions to a vertical cylinder in the cube. The volume fraction in the first case is considered equivalent to the area fraction in the second case for comparison of results. This is a standard assumption in image analysis for estimating volume

fractions from a two-dimensional cut of the solid.[11] Three different proportions of pore volume fraction were studied: 0.11, 0.26 and 0.41. In each case only the matrix is meshed for the calculation. The heat transfer through the pore is assumed to be negligible because $\lambda_p \ll \lambda_m$. The results are shown in Fig. 2c. It can be seen that there is very satisfactory agreement between the computer calculation procedure and the analytical models which is better than ±1%.

Fig. 2c illustrates an important aspect of the approach we are going to apply to real micrographs. The disc in the square is essentially a two-dimensional cut of the sphere in the cube. However the corresponding calculated conductivity, numerical or analytical, is lower than that of the three-dimensional system and underestimates the real conductivity.[12] The difference increases with pore volume fraction and is approximately 10% for $v_p = 0.4$. Despite this drawback, much can be learned.

3.2. Random distribution

A random distribution of discs representing pores in the matrix was then studied using a computer simulation in order to approach a real material more closely. The results are compared with the two analytical models, Eqs. (2) and (3). To create a random distribution of discs, a program developed in our laboratory was used. For each chosen relative density four different random distributions were generated. The discs were attributed with a diameter of 1 mm using the approximation of a monomodal pore size distribution. In order to achieve a satisfactory average for the macroscopic thermal conductivity, the samples were fixed with dimensions of 10 mm width and 20 mm length for the simulation. For each relative density, Fig. 3 shows one of the generated distributions. Fig. 4 then compares the average values of thermal conductivity calculated with these simulations to the predictions of the two analytical models. Even when the discs are randomly distributed in the matrix the Rayleigh model remains valid for pore volume fractions upto 34%. But, since the system becomes even more heterogeneous once the pores become connected (open porosity), typically at 15% pore volume fraction and above, it is a question as to what useful information can be obtained by computer simulation. It is this point which we wish to study in the following part. There does not exist at the present time (to our knowledge), generic software making it possible to create models representing the tortuosity of the pore phase. We thus chose to work directly on micrographs of real porous materials.

3.3. Calculations based on micrographs of real materials

The micrographs used in this work are shown in Fig. 5. For the sample with 89% relative density, only a portion of the original micrograph was chosen for meshing because otherwise the details were too small to be readable by the software. For each meshed image, the thermal conductivity was calculated in a similar way to the simpler geometrical structures of parts a and b. These values are shown in Fig. 6 and compared with the models of Maxwell–Eucken and Rayleigh.

The striking feature of the simulated values for relative density above 80% is the close agreement with the Rayleigh model. In fact this physically makes sense because both approaches concern two-dimensional calculations on isolated inclusions. As the relative density decreases below 80% (higher porosities) the simulated points deviate more and more strongly from the Rayleigh curve. An explanation is based on the increased connectivity of the pore phase, revealed nicely in the black/white images for the 75% and lower relative density samples. The Rayleigh and Maxwell–Eucken expressions are evidently no longer appropriate. A better choice is Landauer's effective medium expression which we can apply to a two-phase system of solid particles and pores. It is given by:

$$\lambda_a = \tfrac{1}{4}[\lambda_p(3v_p - 1) + \lambda_m(3v_m - 1) + ([\lambda_p(3v_p - 1) + \lambda_m(3v_m - 1)]^2 + 8\lambda_m\lambda_p)^{1/2}] \quad (4)$$

where the symbols have the same meaning as previously. The predicted curve is also shown in Fig. 6. The advantage is that the transition from closed porosity to open porosity (percolation of the pore phase) is described. The curve follows first the Maxwell–Eucken curve and then yields significantly lower values of thermal conductivity for relative densities below 85%. In fact examination of the simulated values shows that their general trend follows most closely Landauer's expression even if they are significantly below the analytical curve. Several reasons can explain these differences.

One aspect is that, as mentioned before, the two-dimensional calculation underestimates thermal conductivity values of a three-dimensional system.[12] The other aspects are related to the operation of obtaining a meshed microstructure. First there is the size of the chosen area for study; in other words the magnification of the micrograph. Low magnifica-

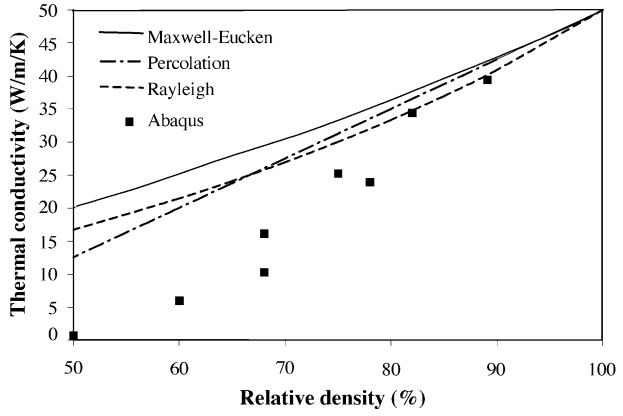


Fig. 6. Comparison of values of thermal conductivity as a function of relative density between the micrograph based numerical simulations and the analytical models.

tion gives a good general view of the structural morphology but decreases significantly the accuracy of the geometrical data in terms of shape of the solid/pore boundaries. There is also the problem of the computer's ability to handle a large data file. High magnification gives precise detail on the shape of the solid/pore boundary but provides less than satisfactory averages for the pore volume fraction and the connectivity of the two phases. These factors are directly involved in the simulation and therefore uncertainty is introduced into the calculated values.

Second, at the present time even with the use of the best compromise between sampling area and structural detail, the meshed microstructures representing the higher pore volume fraction samples (>40%) can exhibit continuous porous zones crossing the entire study area (Fig. 7). The heat flow is completely blocked and this explains the strong decrease in calculated values of thermal conductivity for the highest pore volume fractions shown in Fig. 6.

Another interesting situation concerns the presence of grains which in the two-dimensional cut of the sample are completely isolated by the pore phase. Though, in the reality of the three-dimensional structure of the solid they carry heat, the two-dimensional calculations will just consider them as a part of the porous structure thus decreasing the predicted thermal conductivity value.

Uncertainty and systematic error is not only limited to the thermal conductivity values. Two micrographs taken on the same sample are unlikely to have exactly the same pore volume fractions. This relates to the limited study area size and also to the preparation technique for microscopy where

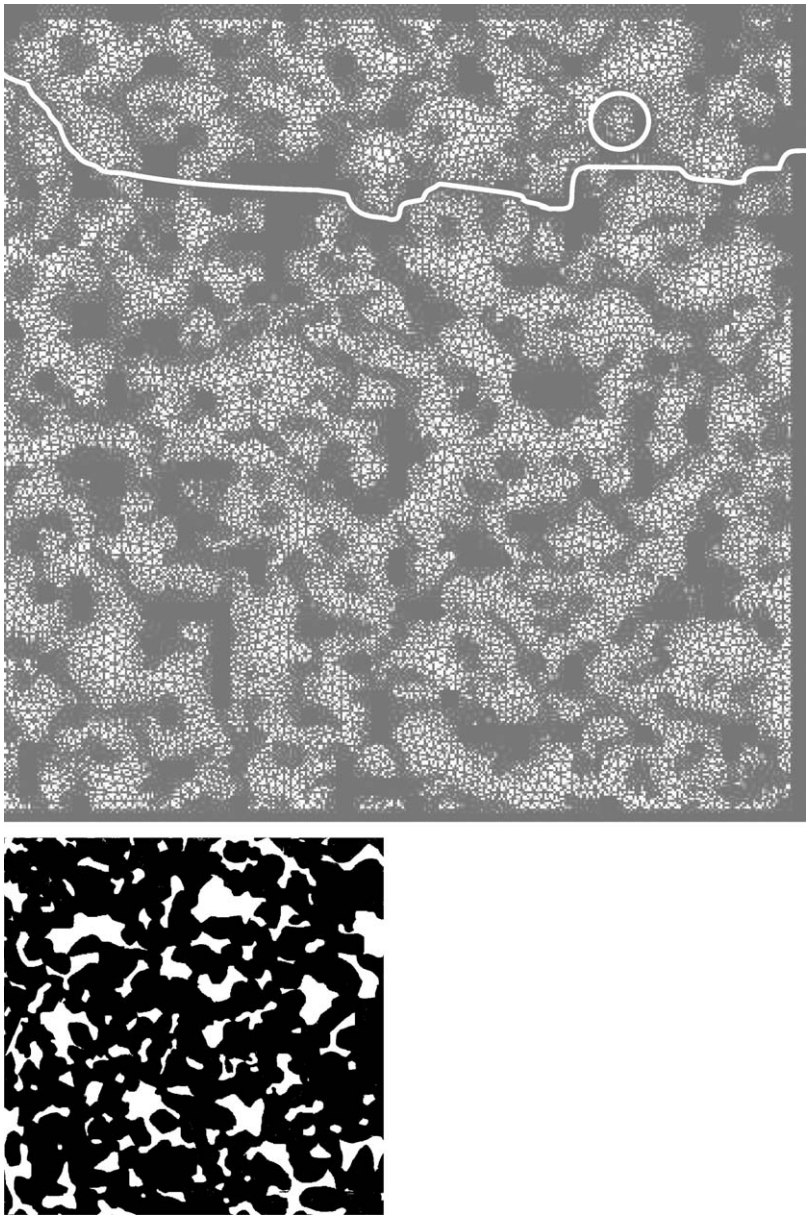


Fig. 7. Calculated temperature distribution obtained for a micrograph of a sample with 40% of pore volume fraction.

grains can be accidentally removed from the sample surface during polishing. Further on, in the process of obtaining meshed microstructures, the setting of the threshold gray level between black and white phases can also remove grains which are poorly defined in the image.

Consequently there is also a measure of uncertainty in the relative density values plotted in Fig. 6.

3.4. Discussion

Up to 20% of pore volume fraction, the results of the numerical simulations are in close agreement with the calculations by the analytical expressions. This validates the technique of observation, digitalization and numerical simulation by the finite element method. The results obtained from micrographs of samples with higher pore volume fractions (40–50%) yield values of thermal conductivity which are too low, but the study is instructive.

The work highlights the influence of the structural morphology of a material (the shape and size of the grains and pores, connectivity of the solid and pore phases) on the value of thermal conductivity. The effects of the transition of the microstructure from one with isolated inclusions to one with more extended and heat blocking porous regions is clearly captured. However it also shows the need to take into account the third dimension for studying heat propagation through a complex material. Ideally the simulations would be performed on three-dimensional structures representing the porous materials. Not having the adequate technique to allow visualization in three dimensions on a microscopic scale, we have directed our study towards the development of software able to generate virtual models of mixtures of many components with random forms and distributions. The objective is to approach most faithfully the real three-dimensional microstructure.

4. Conclusion

Although limited by simplifying assumptions, the analytical models for calculation of the thermal conductivity of heterogeneous materials give rapid and useful estimates for engineers. In this work, we attempted to use a more sophisticated approach in the study of the thermal conductivity of these materials which takes more detailed information on the microstructure into account than the analytical models.

Samples of SnO_2 were made with pore volume fractions up to 50%. Micrographs were then taken and treated by steps involving thresholding and digitalization before writing a data file in international format. The abaqus software, using the finite element method was used to carry out heat flow simulations based on the digitized micrographs and to calculate the apparent conductivity.

Up to 20% of pore volume fraction, good agreement is obtained between the numerical simulations and predictions by the analytical expressions of Maxwell–Eucken and Landauer. In fact in this porosity range, the best agreement is made with the Rayleigh expression, which also physically corresponds to a two-dimensional approach. We point out, as well, that such two-dimensional approaches slightly underestimate the thermal conductivity of a three-dimensional structure. An increasing deviation from the analytical models is then observed above 20% of pore volume fraction yielding thermal conductivity values very close to zero for samples with a pore volume fraction of 50%. The random sampling of the microstructure by the image and the choice of magnification of the micrographs affect the physical representation of the material by the elementary volume used in the simulation and can explain this strong decrease.

Simulations on a three-dimensional structure based on micrographs, taken at successive levels in the sample, would get around these obstacles. However the risk is to generate data files exceeding the memory capacity of the computer even before considering the difficulties related to their treatment. Actually, an emergent idea and solution consists of developing virtual models of materials with mixtures of components defined by random forms and distributions.

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