

Percolation threshold model and its application to the electrical conductivity of layered BaTiO₃-Ni

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The electrical conductivity percolation threshold of the materials composed of conducting particles embedded in a non-conducting host matrix has been investigated. A statistical, numerical method was used, in which the particles are randomly placed, one by one, into the non-conducting host, and the conducting path is searched. The influence of different particle shapes on the percolation threshold is considered. It has been found that, in addition to the anisotropy in the dimensions of particles, the angular distribution of their long axes plays a dominant role in the calculations of the conductivity percolation threshold. Finally, the non-uniform space distribution of positions of particles is taken into account and the model is used to analyze the percolation threshold of the AC conductivity of layered BaTiO₃-Ni composites.

Key words: *conductivity percolation threshold; particle shape; orientational order; layered structure*

1. Introduction

When electrically conducting particles are randomly distributed within an insulating matrix such as metal-ceramic matrix composites, the sample is non-conducting, until the volume fraction of the conducting phase reaches the so-called percolation threshold. In addition, close to the percolation threshold, the electrical properties show a nonlinear (critical) behaviour: small variations in the physical parameters, such as composition, voltage or temperature, result in large variations of electrical properties [1–4]. In order to control the electrical characteristics of such systems, it is very important to have exact knowledge of the percolation threshold. Models using particles of different shapes, mostly spheres, rods and fibres, were employed for the reported calculations of the percolation threshold, not only for electrical conductivity but also for other characteristics of interest. Different models are applied for different particle size distributions [5–9]. Barberg et al. [8] and De Bondt et al. [9] studied the important and more realistic systems of capped cylinders.

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The percolation-threshold volume fraction when the morphology of the conducting phase develops from a spherical to a brick-like shape was studied. The application of the developed model for a rough explanation of the electrical conductivity percolation threshold of a layered BaTiO_3 -Ni composite with ribbon-like microstructures, in the direction perpendicular to the layers [10–12] was required. The rolling-and-folding technique was applied to produce a layered BaTiO_3 -Ni composite with a ribbon-like microstructure. Laminates were obtained by rolling an initial stack of two layers: an insulating one of pure BaTiO_3 and a conducting one in which the volume fraction of doped Ni in BaTiO_3 was 50%, i.e., above the percolation threshold for the layer itself. By repeated folding and rolling several alternating conducting and insulating layers were produced. The width of the laminate at the end of this procedure was the same as the initial pair of layers, so that any single layer was much thinner than at the beginning of the process. The sintered samples with different numbers of foldings were prepared in order to compare the AC electrical conductivity after sintering. The microstructures of the sintered composites were observed using an optical microscope.

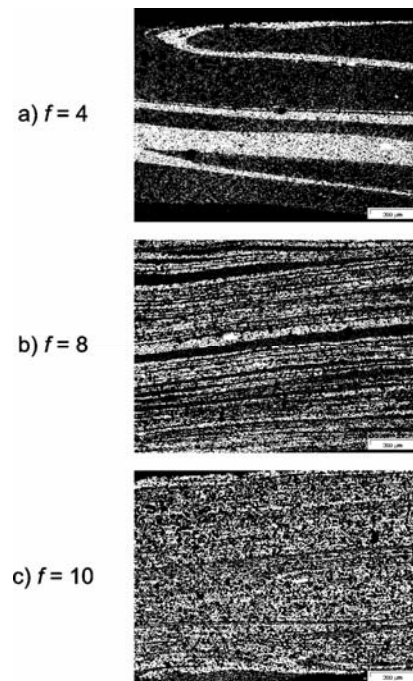


Fig. 1. Microstructure of layered BaTiO_3 -Ni composite after 4 (a), 8 (b) and 10 (c) foldings

One of the interesting features of such composites is the enormous change of the electrical conductivity in the direction perpendicular to the layers, clearly resulting from the development of their microstructure after a sufficient number of foldings f . After $f = 4$ or 5 the layers start to undulate with random phase shifts. This makes it

possible for the nearest conducting layers to adhere and make an electrical contact. Furthermore, the conducting layers even start to disintegrate after $f = 10$. Figure 1 shows the development of microstructure when $f = 4, 8$ and 10 . For $7 < f < 10$ the layers seem to stick together at individual contact points, and this produces the conductivity threshold. After $f = 10$ the conductivity drops as the system is below the percolation threshold.

2. The model

A rectangular cell with dimensions L_x, L_y and L_z , was taken with the plates at $z = 0$ and $z = L_z$, as the electrodes as shown in Fig. 2. Thus the conductivity in the z -axis direction was investigated. Conducting particles in three dimensions with three different shapes: a) spherical (called *spheres*), b) cylindrical rods with half-spheres at the ends (capped cylinders, also called *sticks*), and c) cuboids rounded by half-cylinders and quarter-spheres (called *bricks*) were considered. Mathematical details of the computational procedure are given in [13]. The procedure consists of randomly inserting particles, one by one, into the cell, and checking for the conducting path between the electrodes.

Going from spheres to rounded bricks more parameters and degrees of freedom are needed. For a particular sphere we need three coordinates for the position of its centre and the diameter d of the sphere. The dimensions of a particular stick are given by two variable parameters: the diameter d of the cylinder and spherical caps, and the length-to-diameter aspect ratio: $L/d \geq 1$. In contrast to the spheres, the sticks have two additional degrees of freedom: two angles, θ and ϕ , defining the direction \mathbf{k} of the particle long axis with respect to the z -axis of the system (Fig. 2).

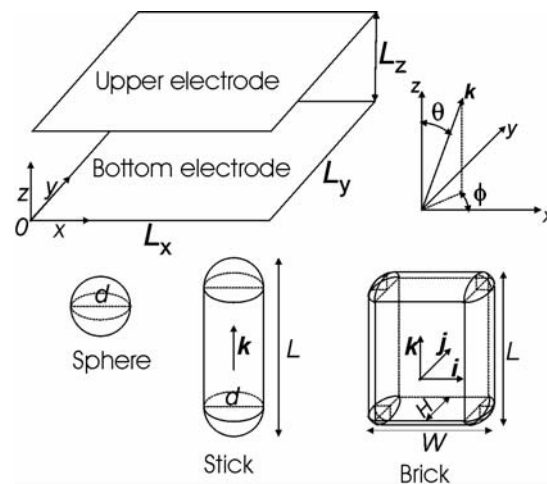


Fig. 2. Coordinate system of rectangular cell and three types of particles. Definition of the directional vectors for non-spherical particles

The dimensions of a particular brick are given by three variable parameters: the width, W , and two aspect ratios: the length-to-width aspect ratio, L/W , and the height-to-width aspect ratio, H/W . $H \leq W \leq L$ was always applied. The bricks have another degree of freedom, the spin angle ψ , which measures the rotation of the particle around its long axis. For computational purposes the three unit directional vectors \mathbf{i} , \mathbf{j} and \mathbf{k} , defining the directions of the edges of the rectangular part of the brick were used (Fig. 2).

In layered composites the distributions of the centres of gravity of particles are non-uniform in the direction perpendicular to the layers. In the simple model, the undulation of layers and study of the “layers” after disintegration were disregarded. An even number of equally thick layers, regarding the odd ones as “conducting” and the even ones as “non-conducting” were taken. When the conducting layers break apart, they are split into smaller conducting objects (rounded bricks, which were taken as the simulation particles), which can rotate in space to some degree and their centres of gravity get redistributed.

3. Results and discussion

The percolation volume v_p for spherical particles was calculated mainly to compare the results with the literature data, to test the reliability of the method, and to adjust some parameters, e.g. the appropriate sizes of particles with respect to the cell dimensions. In the calculations, a typical absolute statistical deviation of the results is 1%. The percolation volume for the sticks depends strongly on the L/d aspect ratio and on the distribution of the long-axis orientation of the particles. The results agree, within the numerical error, with published results [8, 9]. It is believed that this was the first study using rounded bricks. The main conclusions are similar to those for sticks, where for obtaining lower percolation thresholds, larger aspect ratios between dimensions of the bricks are generally advantageous. Also, regarding the distribution of long axes of particles in space (\mathbf{k} -vectors), the results are similar to those for sticks.

It was found that once the particles were long enough (of the order of the layer thickness), the position order/disorder (e.g. the number and thickness of layers, etc.) is not crucial for the percolation volume. What is important, are the aspect ratios of dimensions of particles and their orientational distribution in space as is the case with the non-layered structures. The average orientation of long axes of particles parallel to x -axis was taken, allowing different deviations of individual long axes of particles from this direction. In addition, the spin angle rotations were allowed. For reasonable values of parameters (aspect ratios, etc.) the percolation volumes for bricks are well below 50%, which is enough for conduction, because conducting layers gave 50% of the total layers.

It is concluded that it is quite probable that the electrical conductivity is preserved in the z -axis direction as soon as the layers disintegrate. This contradicts the observation that the percolation threshold is not established after the disintegration of the layers. The most probable answer to this contradiction is that after disintegration of

the conducting layers their pieces also slowly "dissolve". This means that nickel spherical precipitates diffuse out of BaTiO₃-Ni groups into the pure BaTiO₃ phase. Thus, the pieces of the broken conducting layers themselves become nonconducting. On the other hand, the layers after undulation and before complete disintegration ($7 < f < 10$) may be roughly treated as the sticking groups of still-conducting bricks, which also touch the bricks from neighbouring conducting layers, so that the conductivity is established in all directions.

4. Conclusions

Typical percolation volumes for spherical conducting particles in an insulating matrix, obtained with the calculations and reported in the literature (calculations and experiments [6–9]), are between 30% and 40%. With non-spherical particles with a relatively large aspect ratio, much smaller percolation thresholds and, if the particles are at least partially orientationally ordered, anisotropic electric properties are obtained. An alternative and perhaps easier method for achieving similar behaviour is by producing layered composites, including conducting particulate and pure ceramic insulating layers. In this case, the layered BaTiO₃-Ni composite, containing only 25 vol. % of nickel, is considered. By using percolation-threshold numerical method a possible explanation for the behaviour of the electrical conductivity of materials in the direction perpendicular to the layers has been found.

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