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ABSTRACT

The interface effect is taken into consideration, and a special percolation model is proposed for a two-phases metal/ceramic composite in the present paper. The computer simulation shows that the percolation threshold of this interface-controlled percolation behaviour is 4.5% in the three dimensional f.c.c. lattices, which is in good agreement with the experimental data.

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I. Introduction

In recent years many kinds of composites are prepared to obtain special properties that are impossible for the traditional materials. These include metal or metal oxide/polymer composite, ceramic/polymer composite and metal/ceramic composite. The work has been carried out in both of theoretical and experimental on this new field.[1]

In electronic ceramic system, the study of PTC (positive temperature coefficient) thermistor has spanned several branches of materials research. The traditional thermistor prepared from doped $BaTiO_3$ semiconducting ceramics restricted the further applications in high current circuits or devices, because of its high room temperature resistivity(40--100Ωcm).

In a move toward lower room temperature resistivity, several types of thermistor have been developed, such as metal/$BaTiO_3$(PTC semiconducting thermistor) composites, V_2O_3/polymer and carbon black particles/polymer composites.

Many approaches have been applied to investigate the relationship between the electrical properties and its composition. Among them the percolation theory and the effective medium theory are widely used[2,3]. In the previous studies, the two phases of the composites were regarded as two thoroughly independent in a random system and the interface effect were ignored theoretically.

The present paper is mainly concerned with percolation phenomenon theoretically in a system of metal/ semiconducting PTC $BaTiO_3$ ceramic composite by taking into account of the interface effect and a special percolation model is proposed.

II. Physical Model

The previous study showed that the doped $BaTiO_3$ PTC (positive temperature coefficient) semiconducting ceramics consist of conducting grains and insulating grain boundaries that form a barrier to electron flow. The resistivity of the PTC-type $BaTiO_3$ arises from the resistivity of the grain that is about 10^{-2}-10^{-1} Ω•cm and that of the grain boundary that is 10^{1}--$10^{3}\Omega$•cm, the resistivity of the grain boundary is much higher than that of the grains.

In a metal-embedded $BaTiO_3$ semiconducting PTC composite, three types of interface may be distinguished, which are the ceramic grain boundaries, the interface between a ceramic particle and a metal particle and the interface of metal particles. As being described above, the resistivity of the metal-metal interface and the resistivity of the metal powders, as well as that of the $BaTiO_3$ grains are very low, but the resistivity of ceramic grain boundaries is high.

The resistivity of the ceramic-metal interface is dependent upon the height of the Schottky barrier formed at the $BaTiO_3$-metal interface. When the Schottky barrier is far lower than the barrier of $BaTiO_3$ grain boundary, the resistivity of the ceramic-metal interface is low and this type of electrical contact is called ohmic contact, such as the electrical contact of metal Ni-$BaTiO_3$ semiconducting PTC ceramics. Otherwise when Schottky barrier of the ceramic-metal interface is far higher than that of the $BaTiO_3$ grain boundaries, the resistivity of the ceramic-metal is very high and this kind of electrical contact is called non-ohmic contact[6], such the contact of Ag-$BaTiO_3$ semiconducting PTC ceramics interface. If the electrical contact of ceramic and metal is ohmic contact, the resistivity of the ceramic-metal interface can be ignored because of its low resistivity comparing with that of the $BaTiO_3$ ceramic grain boundaries.

Here we deal with a special kind of percolation problem concerning the effect of metal-ceramic interface called interface-controlled percolation. We use Monte Carlo simulation to determine the percolation threshold of this kind of percolation theoretically and then compared it with experimental results.

III. Monte Carlo Procedure

We use 386-type computer to create a sequence of random points (X_i, Y_i, Z_i), i=1, 2, 3, • • • , M. It is supposed that the conducting metal particles with the number of M are randomly distributed in an $N \times N \times N$ three dimensional lattices. After distribution, the random points numbering M are divided into groups. All those particles that can be thought to conduct under certain percolation mechanism are defined to belong to the same group. If one of the coordinate X_i (or Y_i, or Z_i) equals N in a certain group and another corresponding X_i (or Y_i, or Z_i) is 1, a conducting pathway in X (or Y, or Z) direction is forming in the three dimensional lattices.

The problem is focused on the criteria whether the two points are conductive. The ohmic contact case is discussed in the metal/$BaTiO_3$(PTC) composite herein. If one metal particle is at the first-nearest-site of the other, the two metal particles contact with each other, and certainly they are conductive. If one metal particle is at the second-nearest-site of the other metal particle, there is only one ceramic grain particle between the two metal particles. As we assumed above that the resistivity of the ceramic-metal interface is low, in this case the three particles are recognised as conduction because there is no ceramic-ceramic interface with high resistance lying between them (as illustrated in Fig.1). So the connective condition for the interface controlled percolation is that one metal particle with high conductivity is located at the first- or second-nearest site of the other metal particle.

If the x coordinate value of one point is 1 and that of another point is N in one group, a continuous conducting path is forming along the x-axis direction in this random system. Then we change the number M of the high conducting particles, and for each number the computer provides 100 different distributions. And for each distribution the computer judges if there is a continuous conducting path in the system and counts the number of distributions that have a continuous conducting path, then divide it by 100 as the possibility of forming at least one continuous high conducting path. Finally a curve that shows the possibility of the distribution forming continuous conducting pathways as a function of the proportion of high conducting phase is made by the computer. From the curve we can determine the threshold of the interface-controlled percolation problem in several different lattices. We choose the number N as 20 so the conducting particles are distributed in a 20×20×20 lattice.

IV. Results and Discussion.

Using Monte Carlo method, we calculated the percolation threshold of the normal percolation problem and the interface-controlled percolation problem both in three dimensional f.c.c lattices. Fig.2 shows that the calculated percolation threshold is 0.19 for the normal percolation problem, which fit well with the well-known result[7,8]. For the interface-controlled percolation behaviour the calculated threshold is 0.045 for f.c.c. lattice, which is shown in Fig.3. The composition dependence of resistivity in the Ni/$BaTiO_3$(PTC) composite was investigated experimentally, and the observed percolation threshold was about 5% (volume fraction of Ni)[9]. The prediction of percolation threshold by Monte Carlo simulation is in excellent agreement with the experimental result. For the electrical contact between $BaTiO_3$ PTC ceramics and metal Ni is ohmic, the experimental result of the nickel metal powder/$BaTiO_3$ semiconducting PTC ceramic composite is well explained by the above interface-controlled percolation model, implying that the continuous conducting pathway begins to form when the Ni volume fraction is *only* 5%[9] *both experimentally and theoretically*.

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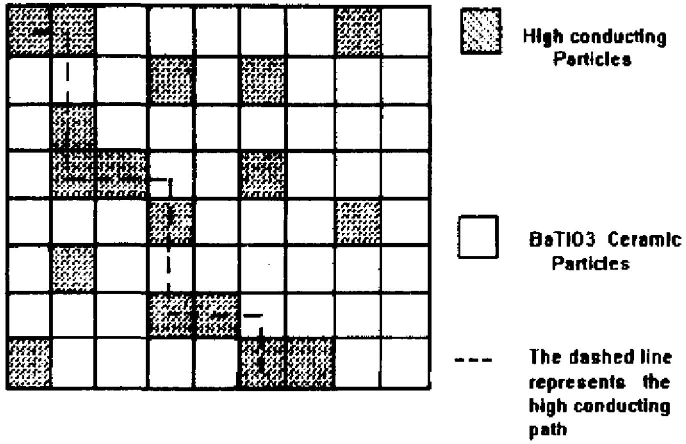

Fig.1

An illustration of forming a continuous conducting pathway in an interface-controlled percolation system

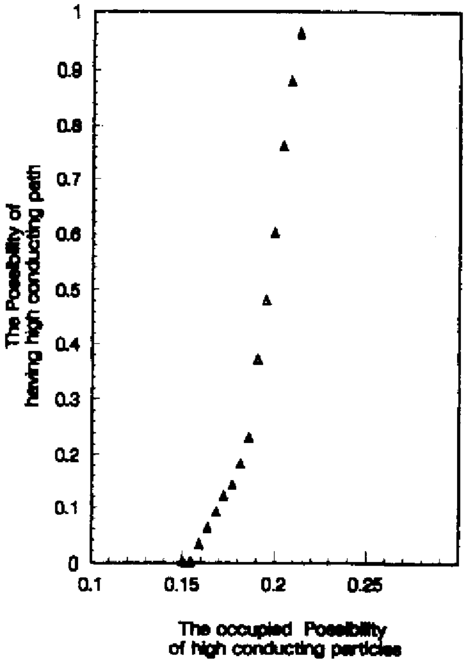

Fig.2

Calculated conductive possibility as a function of the proportion of the conducting phase in f.c.c. three dimensional lattice of normal percolation system

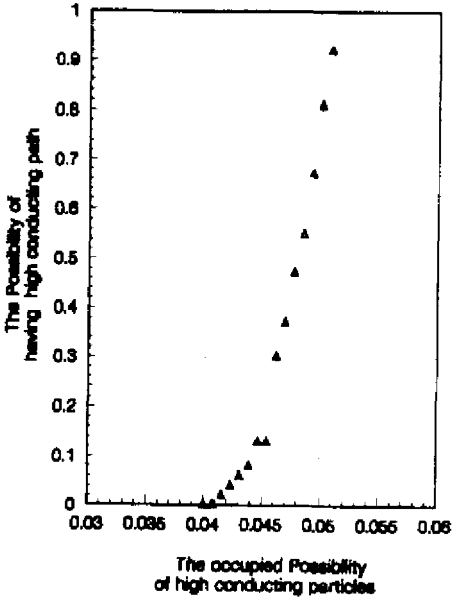

Fig.3

Calculated conductive possibility as a function of the proportion of the conducting phase in f.c.c. three dimensional interface-controlled percolation system