Composites Part B 92 (2016) 377–383

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Thermal conductivity determination of conductor/insulator composites by fractal: Geometrical tortuosity and percolation

Li-Chao Feng [a, c, d], Ning Xie [b, c, *], Wen-Zhu Shao [c, **], Liang-Xing Lu [c], Liang Zhen [c], Jie Zhao [d]

[a] School of Mechanical Engineering, Huaihai Institute of Technology, and Jiangsu Marine Resources Development Research Institute, Lianyungang 222005, China
[b] School of Materials Science and Engineering and Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan, Shandong 250022, China
[c] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[d] School of Mechatronics Engineering, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
19 January 2016
Accepted 18 February 2016
Available online 26 February 2016

Keywords:
A. Ceramic-matrix composites
B. Thermal properties
C. Analytical modelling
E. Sintering
Fractal characterization

ABSTRACT

The thermal conductivity prediction of a conductor/insulator composite with various geometrical structures of the conducting phase is one of the top challenges in disordered composites. To determine the effects of the geometrical structure of the second phase on the thermal conductivity of a conductor/insulator composite, Cu_2O/Cu composites were prepared with spherical or branch-like Cu by hot-pressing technology. The box-counting fractal dimension was applied to characterize the geometrical structure of the second phase. The fractal dimension of branch-like Cu shows significantly lower values than the spherical Cu with a same filling content. The fractal dimension increasing rate with increasing Cu content was first introduced to predict the thermal conductivity of the composites. These results provide a pathway to determine the effects of the geometrical structure of the second phase on the thermal conductivity and shed some lights on building relationships between the tortuosity, fractal dimension, and overall performances of conductor/insulator composites.

1. Introduction

Although conductor/insulator composites are promising materials which have been widely used in various fields, such as electrodes for lithium ion batteries and solid oxide fuel cells [1], inert anode materials for Al production [2,3], solar energy conversion [4], anti-corrosion coating under marine environment [5], sensors [6], catalysts [7], and supercapacitors [8], how to accurately predicting the relationship between microstructures and macro properties is still one of the top challenges for the composites in which the second phases are randomly embedded in the matrix phase.

The critical transport phenomenon, as a specific behavior of the dual-phase disordered conductor/insulator composites, is largely governed by the geometrical microstructure of the second phases [9]. Percolation, as the main theory describing the critical transport phenomenon of disordered materials, was widely studied in the past decades. Two milestone models, namely the *tunneling* model and the *Swiss Cheese* model, were developed by Balberg [10] and Halperin [11], respectively, to analyze the critical exponents for the electrical conductivity, elastic constants, and fluid permeability near the percolation threshold of a class of disordered continuum systems. Recently, numerical methods to predict the effective physical properties of complex multiphase materials has been reviewed by Wang and Pan [12]. In that work, the critical transport phenomena, such as the electrical conductivity, thermal conductivity, dielectric permittivity, and elastic moduli, were systematically summarized. In addition, the main factors, including the size, anisotropy, morphology, and phase interaction, which affect these physical properties were summarized as well. Hunt [13] systematically studied the tortuosity and the percolation paths in dual-phase systems, in which the fractal was applied as a promising approach to describe the transport property of these systems.

---

[*] Corresponding author. School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China.
[**] Corresponding author.
E-mail addresses: xiening@hit.edu.cn (N. Xie), wzshao@hit.edu.cn (W.-Z. Shao).

http://dx.doi.org/10.1016/j.compositesb.2016.02.046
1359-8368/

As one of the most important critical transport phenomena, the heat transport in disordered dual-phase composites has been widely studied in recent years [14–19]. Many numerical studies have been developed to predict the thermal conductivity as a function of the filling content of the second phase. Maxwell model [20], one of the most widely accepted methods, claimed that the thermal conductivity of disordered dual-phase composites could be predicted as:

$$\rho_{mix} = \rho_{const} \frac{1 + 2\theta - 2f(\theta - 1)}{1 + 2\theta + f(\theta - 1)} \tag{1}$$

where ρ_{mix} is the thermal conductivity of the composite, θ is the ratio of the thermal conductivity of the continuous phase and the dispersed phase, ρ_{const} and f are the thermal conductivity and the volume or filling fraction of the dispersed phase, respectively. One thing has to be noted in this equation is that the dispersed phase is the thermally conducting phase and the continuous phase is the thermally insulating phase. Another famous description is the series/parallel model [21]:

$$\rho_{mix(p)} = \rho_d f_d + \rho_c f_c \tag{2}$$

$$\rho_{mix(s)} = \frac{\rho_d \rho_c}{\rho_d f_c + \rho_c f_d} \tag{3}$$

where ρ_{mix} is the thermal conductivity of the composite, ρ_c and ρ_d are the thermal conductivities of the continuous phase and the dispersed phase, and f_c and f_d are the volume or filling fraction of the continuous phase and the dispersed phase, respectively.

Recently, an analytical model based on experimental results was presented to predict the thermal conductivity of hybrid carbon nanotubes(CNT)-graphene(GR)/epoxy composite, which build a bridge to connect the hybrid structure of the second phase to the thermal conductivity of the composite [22,23]. In this model, the thermal conductivities of the CNT and the GR were both considered, and the final thermal conductivity of the CNT/GR/epoxy hybrid composites can be predicted as:

$$\frac{\rho_{mix}}{\rho_e} = \frac{1 + f_c \frac{\left(\frac{\rho_c}{\rho_e}\right)}{3} + \frac{2\left(f_g - 0.001\right)^{\alpha}\left(\frac{\rho_g}{\rho_e}\right)}{3}}{1 - \left(2f_c + f_g\right)/3} \tag{4}$$

where ρ_{mix}, ρ_c, ρ_g, and ρ_e are the thermal conductivities of the composite, CNT, GR, and epoxy, respectively, and the f_c and f_g are the volume fractions of the CNT and the graphene. In this model, the percolation threshold f_c was estimated as 0.001, and the value of the α, which is defined as the critical conductivity exponent based on percolation theory [13,24], was determined as 0.87 by experimental results corresponding to $f_g < 0.043$.

Although the above mentioned models have considerably contributed the development of the relationship between the filling content and the thermal conductivity of dual-phase disordered composites, the effects of the geometrical microstructure on the thermal conductivity was not presented clearly. It has been widely accepted that, near the percolation threshold, the critical transport properties obey the power law [25], and the geometrical structure of the second phase exhibits a self-similarity in a scale range and is able to be determined by fractal dimensions [26]. Numerical works demonstrated the self-similar nature of the infinite clusters with fractal dimension of $D \approx 1.9$ and 2.5 and the optimal path in the infinite clusters with fractal dimensions of $D \approx 1.22$ and 1.43 in two and three-dimensional lattices, respectively [27]. Some studies have shown that the thermal conductivity of composite materials can be characterized by fractals of the second phase embedded in the matrix materials [28]. Yu and Li studied the effective thermal conductivity of composites with embedded H-shaped fractal-like tree networks. In this study, it was found that the thermal conductivity decreases with increasing length of the branches and decreasing successive branch diameter ratio and the density of the network [29]. Cervantes-A'lvarez also claimed that the thermal conductivity have a straight relationship with the fractal structure of the second phase in composites [30].

Although these models and methods have successfully opened some gates of thermal conductivity prediction in disordered dual-phase composites, the effect of the geometrical microstructure of the second phase, which represents the real transport paths in a dual-phase composite, on the thermal conductivity is still the most challenging topic in disordered materials. Unlike the electrical transportation, the thermal transportation is not able to be reflected by simply applying the power law or the fractal dimension due to the percolation phenomenon is less visible in the system [31]. Therefore, it is necessary to develop an effective method to determine the thermal conductivity as a function of the filling content and the geometrical microstructure of the second phase, in which how to quantitatively characterize the geometrical microstructures of the second phase plays the key role to realize this method. In this study, Cu/Cu_2O composites were prepared with branch-like and spherical Cu powders with size of 15 and 75 μm, and a simple model was developed based on fractal method to build the relationship between the thermal conductivity and the geometrical microstructure along with the filling content of the second phase.

2. Experimental

The Cu/Cu_2O composite were prepared via hot pressing technology. Branch like and spherical Cu with size of 15 and 75 μm were used for preparing the final materials. The purities of Cu_2O and Cu are 99.8% and 97% respectively. Fig. 1 showed the SEM morphology of branch like and spherical Cu powders. For preparing the disordered composites, the Cu and Cu_2O powder were ball-milled in dehydrated ethyl alcohol for 12 h and subsequently dried in a vacuum furnace at 80 °C. After drying, the mixture powders were heated to 1050 °C at a heating rate of 20 °C/min, followed by hot-pressing with 25 MPa and a 40 min soak in a graphite mold. The furnace chamber was purged with 1.0 atm of argon gas from the start of the hot-pressing procedure. The thermal conductivities were measured on NETZSCH-M3-LAUDA with the surface and bottom temperatures of 60 °C and 30 °C respectively. The box-counting fractal dimension of the prepared composites was determined from the binarized optical microscopy (OM) image of the composites, shown as Fig. 2. It was calculated from a space in which the binarized pattern is embedded. In this space, a set E was covered by a grid with a pixel (i.e., picture element) length δ, and the number of pixels $N(\delta)$ that intersect E was counted. The box-counting fractal dimension D_b is able to be calculated as $\lim\limits_{\delta \to \infty} \frac{\log N(\delta)}{\log(\delta)}$. Based on this definition, the slope of the fitted straight line segment in the log–log plot was defined as the fractal dimension of the image. For the *dc* electrical conductivity test, the specimens were cut into a bar shape with a size of 1 mm × 2 mm × 20 mm, and measured at room temperature with a 4-probe technique [25].

3. Results and discussions

In a lattice percolation system, the infinite cluster can be divided into two main structures, namely the “backbone” and the “dangling