Applicability Study of Classical and Contemporary Models for Effective Complex Permittivity of Metal Powders

Erin M. Kiley and Vadim V. Yakovlev
Department of Mathematical Sciences
Worcester Polytechnic Institute
Worcester, MA, USA
vadim@wpi.edu

Kotaro Ishizaki and Sébastien Vaucher
Laboratory for Advanced Materials Processing,
EMPA – Swiss Federal Laboratories for
Materials Science and Technology, Thun, Switzerland
Sebastien.Vaucher@empa.ch

***Abstract*—Microwave thermal processing of metal powders has recently been a topic of a substantial interest; however, experimenttal data on the physical properties of mixtures involving metal particles are often unavailable. In this paper, we perform a systematic analysis of classical and contemporary models of complex permittivity of mixtures and discuss the use of these models for determining effective permittivity of dielectric matrices with metal inclusions. Results from various mixture and core-shell mixture models are compared to experimental data for a titanium/stearic acid mixture (obtained through the original measurement) and a tungsten/Teflon mixture (from literature). We identify Bruggeman's and Buchelnikov's models to be the most accurate from each category for volume fractions below percolation.**

Keywords—core-shell model, effective complex permittivity, metal powder, mixture model, percolation threshold.

I. Introduction

Microwave (MW) thermal processing of materials is gaining increasingly more attention as an interdisciplinary technology for volumetric heating, which has the potential for substantial energy savings. As a multiphysics phenomenon, MW heating is known to be complex and difficult to control. It has recently become evident that computer modeling could help clarify many issues involving interaction of microwaves with materials and suggest engineering solutions for designing efficient MW systems. Major progress has been made due to the development of computational schemes based on implementation of coupled electromagnetic-thermal models (e.g., [1-4]). Recently, attempts to couple electromagnetic and thermal solvers with tools for modeling associated kinetic transformations [5] and mechanical deformations [6] have been reported as initial steps toward a comprehensive modeling technique for MW sintering. However, regardless of the level of accuracy of the numerical techniques and the degree of idealization applied, the adequacy of the model depends to a great extent on the quality of input data on material parameters.

This study is motivated by the acute need for data on electromagnetic parameters for use in multiphysics modeling of MW processing of materials. While reports on measurements of the dielectric constant and loss factors of dielectric materials are prevalent, data on the effective complex permittivity of metal powders is very limited; also, in the literature, conflicting values (sometimes up to orders of magnitude) can be found [7]. This paper aims to draw more attention to the potential applications of some classical and contemporary models for determining complex permittivity of composites/mixtures that might be applicable to metal powders. We briefly review most notable models, present them in closed form, examine the ranges of validity of their input parameters, and discuss their applicability with reference to our original measurements of effective complex permittivity of a mixture of titanium/stearic acid and the results by Zimmerman *et al.* [8] in determining the loss factor of a tungsten/Teflon mixture. We discuss the reasons for discrepancies between the results obtained from the models and the experiments. Under the identified limitations for their use, the classical Bruggeman mixture model and the core-shell mixture model recently proposed by Buchelnikov *et al*. [9, 10] are shown to be the ones producing most plausible results for the powders whose volume fraction is below the percolation threshold.

II. Review of the Models

A. Lichtenecker's Logarithmic Mixture Formula

Lichtenecker's mixture formula has been used to calculate complex permittivity of various mixtures of dielectric substances. Lichtenecker and Rother presented the formula in its logarithmic form [11], which can be reformulated to compute the effective permittivity most efficiently as follows:

$$\varepsilon_{eff} = \prod_{n=1}^{N} \varepsilon_n^{\alpha_n},$$

where the ith component of the N substances comprising the mixture is said to have effective permittivity ε_i and volume fraction α_i. When this model is used for estimating $\varepsilon_{eff} = \varepsilon' - j\varepsilon''$ of a mixture, where the ith component is a metal powder, then ε_i should represent the effective conductivity of the metal powder in air.

Recently, Simpkin derived Lichtenecker's formula directly from Maxwell's equations and the principle of charge conservation under the assumption of a random spatial distribution of shapes and orientations of inclusions in a dielectric mixture [12]. This characterization indicates that the closer the spatial distribution of components is to being random, the more accurate will be Lichtenecker's approximation of effective permittivity.

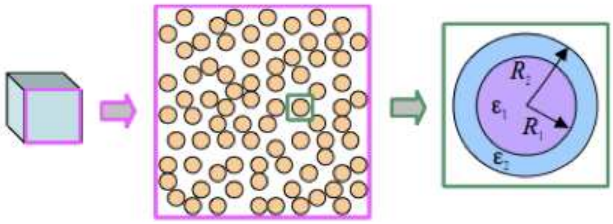

Figure 1. Core-shell powders of the type described in the model by Buchelnikov *et al.* [9, 10]

B. Maxwell Garnett Mixing Rule

The Maxwell Garnett formula was originally developed to determine the optical properties of a particular glass substance that contained minute spherical particles of gold [13], and as such, is suitable to describe mixtures involving metal particles, provided that those mixtures satisfy validity conditions discussed below. The formulation for a mixture of two materials is as follows:

$$\varepsilon_{eff} = \varepsilon_1 \frac{\varepsilon_2(1+2\alpha)-\varepsilon_1(2\alpha-2)}{\varepsilon_1(2+\alpha)-\varepsilon_2(1-\alpha)}$$

where α is the volume ratio of the embedded material, ε_2 is the permittivity of the embedded material, and ε_1 is the permittivity of the matrix material.

In general, the model is valid for mixtures that are electrodynamically isotropic, with parameters that do not depend on the intensity of the electric field and do not change in time, with inclusions that are small compared to the wavelength and are separated by distances greater than their size, and with inclusions, if they are conducting, at a concentration lower than the percolation threshold [14].

Also, Simpkin [12] has shown that, under the condition that the value $2\alpha(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)$ is small, the Maxwell Garnett equations may be derived as an approximation to Lichtenecker's formula.

C. Bruggeman's Symmetric Mixture Formula

Bruggeman's symmetric mixture formula for a two-part mixture, introduced in [15], is:

$$\alpha\left(\frac{\varepsilon_1-\varepsilon_{eff}}{\varepsilon_1+2\varepsilon_{eff}}\right)+(1-\alpha)\left(\frac{\varepsilon_2-\varepsilon_{eff}}{\varepsilon_2+2\varepsilon_{eff}}\right)=0.$$

This formula is quadratic in ε_{eff} and always has a positive discriminant together with a strictly negative root; in order to be a solution, the other root must be positive, which motivates the restriction that

$$\varepsilon_1(2-3\alpha)\le\varepsilon_2(1-3\alpha)+\sqrt{(\varepsilon_1(2-3\alpha)+\varepsilon_2(3\alpha-1))^2+8\varepsilon_1\varepsilon_2}$$

The results produced by Bruggeman's formula should be verified, and it should be determined that this restriction is, in fact, satisfied. If not, then a different model should be used.

D. Buchelnikov's Model for Core-Shell Powders

The model introduced by Buchelnikov *et al*. [9, 10] considers spherical core-shell particles randomly distributed in the effective medium. This model is developed specifically for metal powders, and to this end takes into account the presence of the oxide layer that forms on particles of metal, resulting in core-shell type particles of the kind shown in Fig. 1. The authors determine the following relationship between the effective permittivity of the mixture and the radii of the spherical inclusions:

$$\alpha\varsigma\frac{\varepsilon_2\left[3\varepsilon_1+(\varsigma-1)(\varepsilon_1+2\varepsilon_2)\right]-\varepsilon_{eff}\left[3\varepsilon_2+(\varsigma-1)(\varepsilon_1+2\varepsilon_2)\right]}{2a\varepsilon_{eff}+b\varepsilon_2}+$$
$$+(1-\alpha\varsigma)\frac{\varepsilon_g-\varepsilon_{eff}}{\varepsilon_g+\varepsilon_{eff}}=0,$$

where ε_g is the permittivity of the gas or vacuum, $\varepsilon_{1,2}$ are the permittivities of the metallic core and shell respectively, and the expressions for ζ, a, and b are:

$$\varsigma=(R_2/R_1)^3=(1+l)^3,\qquad l=(R_2-R_1)/R_1,$$
$$a=(\varsigma-1)\varepsilon_1+(2\varsigma+1)\varepsilon_2,\quad b=(2+\varsigma)\varepsilon_1+2(\varsigma-1)\varepsilon_2$$

where $R_{1,2}$ are the radii of the metallic core and shell respectively. In the limiting cases $R_1 \to 0$ and $R_2 \to R_1$, Buchelnikov's model reduces to exactly the Bruggeman equation.

E. Other Models

Also considered in this study were models by Ignatenko *et al.* [16], a variation of the Lichtenecker formula by Neelakantaswamy *et al*. [17], and variations of the Maxwell Garnett formula to account for inclusions of multiple types. These versions may indeed make the models discussed more complete, but do not appear to impact our consideration of metal powders in particular.

III. Experimental Results

In this section, we describe the results of two experimental attempts to evaluate the effective complex permittivity of mixtures involving metal powders. The results of these experiments are used to test some of the models described above.

A. Tungsten / Teflon Mixture

In [8], Zimmerman *et al*. dealt with the samples of powders made with varying volume fractions of tungsten in Teflon powder. The mixtures were formed into cylindrical pellets with varying particle sizes, and the authors determined the effective complex permittivity and permeability of each sample using cavity perturbation techniques.

B. Titanium / Stearic Acid Mixture

In our experiment, we mechanically mixed gas atomized titanium particles (spherical, 25 microns, Pyrogenesis, Canada) with stearic acid (Aldrich, 95%) in various volume fractions. These mixtures were compacted uniaxially into cylindrical pellets of diameter 10 mm and height 20 mm. The cavity perturbation formalism was assumed valid and applied to extract the effective complex permittivity from the frequency shift and the quality factor.

IV. Models versus Experiments

The experiments mentioned in the previous Section have produced the results that we use to test the mixture and core-shell mixture models reviewed in Section II.

A. Mixture Models

Taking the effective complex permittivity of tungsten to be 30 + *j*8 [18], and the complex permittivity of Teflon 2.29 + *j*0.03 [19], we use the Lichtenecker, Maxwell Garnett, and Bruggeman models to reconstruct the dielectric constant and the loss factor of the titanium/Teflon mixture for different α. These curves are shown in Fig. 2(a).

The determined material properties exhibit distinct percolation behaviors, characterized by a peak in tanδ = $\varepsilon''/\varepsilon'$ at volume fractions which depend on the average particle size of the mixtures. The location of this peak is shown in Fig. 2(b) by the approximate values of tanδ for particles of diameter 2.3 microns, alongside the same tanδ predicted by the mixture models.

Assuming that ε' and ε'' are smooth functions of volume fraction, a peak in tanδ may occur only at those critical volume fractions α_p for which the first derivative of tanδ is zero; that is,

$$\varepsilon''(\alpha_p)\frac{d\varepsilon'(\alpha_p)}{d\alpha} = \varepsilon'(\alpha_p)\cdot\frac{d\varepsilon''(\alpha_p)}{d\alpha}.$$

Using the expression for complex permittivity predicted by Lichtenecker's model, this situation occurs independently of volume fraction when $\varepsilon_1'\varepsilon_2' = \varepsilon_1''\varepsilon_2''$, and in this case, all subsequent derivatives of tanδ are zero—so no peak occurs for any mixture whose permittivity is treated by the Lichtenecker model. Using the expression predicted by the Maxwell Garnett model, no zeros of the first derivative of tanδ exist for any mixture. The Bruggeman model, applied to the mixture of tungsten and Teflon, also did not predict any peaks in tanδ, so it could be concluded that none of those models could be accurate for predicting percolation behavior of the tungsten/Teflon mixture.

B. Core-Shell Models

The effective complex permittivity of core-shell titanium particles in a stearic acid matrix was computed using Buchelnikov's model, and the complex permittivity of the titanium and stearic acid mixture, ignoring the presence of the titanium oxide layer, was computed using various mixture models, with the results shown in Fig. 3. Values used for the effective complex permittivity of titanium and the complex permittivity of stearic acid were taken directly from the experiment.

Since the radius of the oxide layer on the titanium particles is a necessary input to Buchelnikov's formula but is not known for the titanium particles we study, this parameter was chosen through golden selection search and parabolic interpolation to be the one which produced the permittivity curve closest to the experimentally obtained data.

In our experiments, the measured material properties also exhibit distinct percolation behaviors, where both ε' and ε'' of the mixture exceed the values of the corresponding parameters

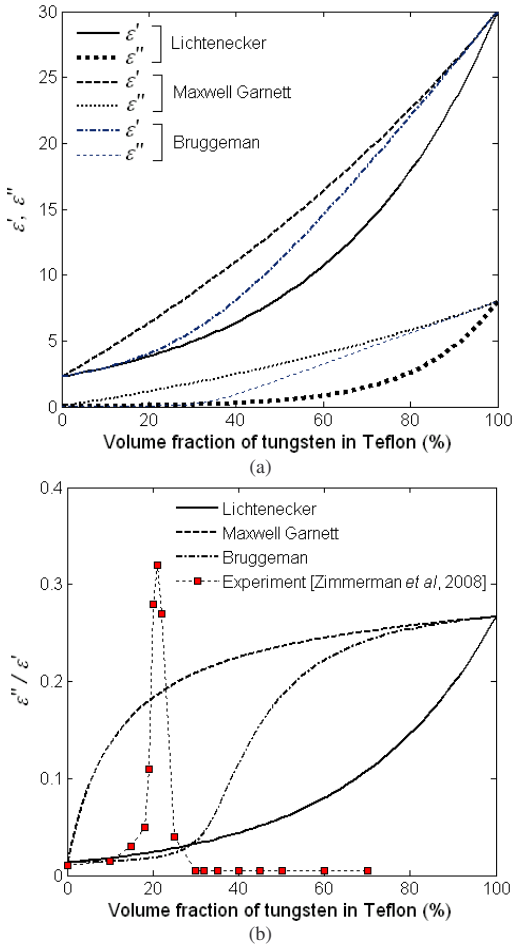

Figure 2. Complex permittivity (a) and tanδ (b) of tungsten/Teflon mixture – models and measurement.

for stearic acid and for tapped titanium powder. However, it is seen that neither the core-shell mixture nor the conventional mixture models are capable of accurately predicting permittivity at volume fractions beyond the percolation threshold of the mixture. Yet, it should be noted that before the percolation threshold, all of the curves predicted are a good fit to the experimental data obtained. The minimum error taken using only the first five data points (that is, those before the percolation threshold) is 0.441 (using Buchelnikov's model) for the ε' curve, and 0.101 (using Bruggeman's model) for the ε'' curve.

V. Conclusions

We have presented and discussed various models, of both the mixture type and the core-shell mixture type, for determining the effective complex permittivity of inhomogeneous materials. These models have been tested against experimentally measured effective complex permittivity of mixtures of metal particles with dielectrics. We have shown that the Bruggeman, Lichtenecker, and Maxwell-Garnett models do not correctly predict percolation behavior, but before the percolation threshold, Buchelnikov's and Bruggeman's models

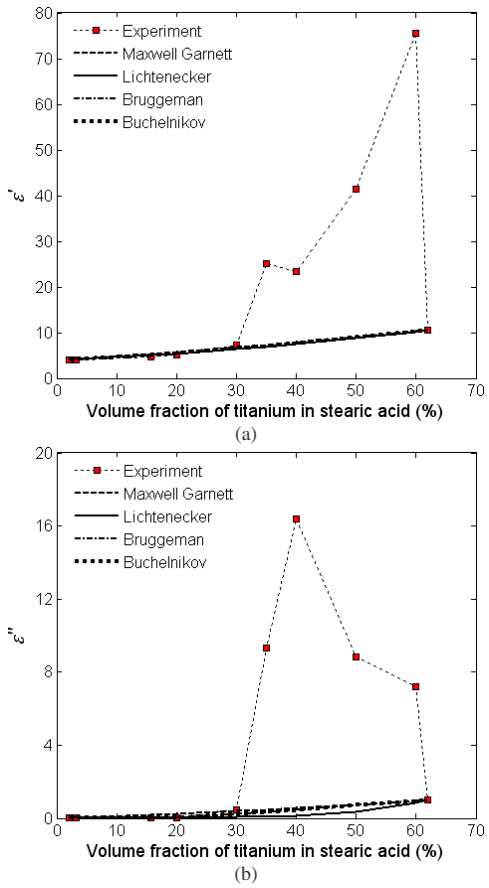

Figure 3. Real (a) and imaginary (b) parts of effective complex permittivity of titanium/stearic acid mixture – models and experiment.

do the best job of quantitatively predicting ε_{eff} of a titanium/ stearic acid mixture. Indeed, the continuum approximation that is valid for dielectric mixtures is applicable only below the percolation threshold of the conductive phase. Beyond this limit, discrete models might be more appropriate. It has been also illustrated that Buchelnikov's core-shell type model also accounts accurately for the oxide layer that may occur on particles of metal powders.

Finally, it is worth mentioning that a generalization of some of the discussed mixture-type formulas, together with a full discussion of Weiner limits and Hashin-Shtrikman bounds, appears in [20], and may be most useful for researchers seeking a model that accurately fits measured data.

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