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Modelling the spectral selective solar absorption properties of graphite–silica composite/aluminium structures

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ABSTRACT

Calculation of the index of refraction of graphite–silica composites has been performed using Bruggeman's theory for randomly oriented nano-graphite grains in silica. Subsequently the normal incidence reflectance from graphite–silica composite/aluminium and anti-reflection coating/graphite–silica composite/aluminium structures was performed using the transfer matrix formalism. The solar performance (absorptance, emittance, and efficiency) of the graphite–silica composite/aluminium structures is calculated with respect to composition and thickness of the graphite composite layer (and presented in the form of contour plots) and is compared with experimental data. We show that the combined contour plots are consistent with experimental data only within a small range of volume fraction and thickness of the composite layer. Further, we present analytic relations for the near optimal index of refraction and thickness of the anti-reflection coating for the graphite–silica composite/aluminium structure.

1. Introduction

Spectral selective solar absorbers (SSSAs) can be achieved in several ways, where one of them provides an advantage in flexibility and production costs and is produced by using a solar absorbing layer on top of a highly reflective metal surface (tandem structure) [1]. Theoretical calculations predicted early that single layer absorbers on metals can have high fraction of solar irradiance absorbed, i.e. absorptance (α), with small emittance (β) values as long as the refractive index and extinction coefficient values are within certain limits [2]. One flexible way of controlling the optical properties of materials is by incorporating inclusions of one phase, e.g. a metal, into another, e.g. a ceramic, forming a composite, which were used already in commercial SSSAs in the 70s, e.g. "black chrome" and nickel-pigmented anodic Al_2O_3 [3]. While carbon and graphite layers on metals were investigated in the 70s as potential SSSA candidates [4,5], it is only recently that experimental work on carbon based composite tandem structures have been realised that show high absorptance, although the dependence of solar performance of the SSSA, e.g. efficiency (η), on the microstructure and composition of the composite was not revealed [6,7]. In this work we will use a theoretical framework for investigating in more detail the structural and compositional requirements for optimisation of η of graphite–silica composite/Al SSSAs.

2. Method

The first part of this section will describe the methodology for determining the complex dielectric constant (ε) of the graphite–silica composite and the second part will describe how the reflectivity and associated α, β and η values of composite/metal structures are calculated in a similar way as previous work [8].

The optical properties of composites attracted the interest of Maxwell Garnett more than a century ago as a keystone for the interpretation of the colour of glasses with metal inclusions. Noteworthy, the Maxwell Garnett (MG) theory assume that inclusions are completely surrounded by the matrix, which is plausible when the volume fraction (f) of the inclusions is significantly smaller than the matrix, but becomes less probable as f increases. This suggests that MG theory is unlikely to give a reliable description of the optical properties of composites for high f values in the absence of microstructural information. However, the Au–silica system, which exhibits a transition from a state where the metal is included to a state where the metal can be considered the medium, has been modelled well for $0 < f < 1$ using MG theory where below and above a threshold in f (~0.4) Au and silica, respectively, was the phase of inclusions [9].

An alternative to this theory was developed by Bruggeman, which is applicable for $0 < f < 1$ and is likely to give a better description for high f-values in the absence of microstructural information. In this work, we shall use the Bruggeman theory to calculate the optical properties of graphite–silica composite/Al SSSAs.

The Bruggeman theory assumes that each phase may be considered to be in a matrix with an effective dielectric constant ε_c [10]; hence the polarisation of a sphere of the i:th phase is given by (using the Claussius–Mossotti relation):

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$$P_i = E_{loc} a_i^3 (\varepsilon_i - \varepsilon_c)/(\varepsilon_i + 2\varepsilon_c) \quad (1)$$

where E_{loc} is the local field and a_i is the radius. If $E_{loc} \sim E$ (the macroscopic applied electric field) the total polarisation, (P), $P = \sum P_i N_i$ (where N_i is the concentration of i-type spheres) must equal zero, which gives the following equation: $\sum f_i (\varepsilon_i - \varepsilon_c) / (\varepsilon_i + 2\varepsilon_c) = 0$. This equation is solved with respect to ε_c, where the summation is for i = 1,2,3.. s, where s is the total number of phases. It should be noted that for low *f*, MG and Bruggeman theory (for a binary phase) yield nearly identical results, while at larger *f* a significant difference may develop (as for the Ag–silica composites) [11,12].

The value of ε of a material is a property that is either a scalar (for a macroscopic isotropic solid) or a tensor for a non-isotropic solid. The physical properties of graphite, a solid with a single symmetry axis (c-axis), are in general anisotropic, including its ε-value (ε_g). Thus, ε_g and $\varepsilon_g^{||}$, which are complex numbers with a real and an imaginary part, describe the polarisability when the electric field is oriented perpendicular and parallel to the c-axis, respectively. The dependence of the dielectric constant of graphite on wavelength used in this work was obtained from tabulated values [13]; it should be noted that while experimental determination of ε_g has been obtained accurately over the full wavelength range of interest in this work, reported experimental $\varepsilon_g^{||}$ values vary significantly depending on experimental procedure [14]. The uncertainty in the $\varepsilon_g^{||}$ values from optical spectroscopy is mainly due to problems of obtaining a smooth surface.

In order to emulate polycrystalline graphite, where grains are randomly oriented, ε_g and $\varepsilon_g^{||}$ need to be mixed in proper proportions. Previous work suggest that the optical properties of pure polycrystalline graphite material (100 nm < λ < 500 nm) are well described using the Bruggeman theory and with volume fractions of 2/3 and 1/3 for the associated ε_g and $\varepsilon_g^{||}$ values, respectively [15]. Thus with these proportions, the magnitude of uncertainty in $\varepsilon_g^{||}$ (as discussed previously) will have a small impact on the uncertainty of the effective ε-value of a poly-graphite composite since ε_g is much larger than $\varepsilon_g^{||}$. Thus, this work reports on the calculations using Bruggeman theory for mixtures of ε_g and $\varepsilon_g^{||}$ in the proportions 2/3 and 1/3, respectively, dispersed in silica (ε_{SiO2}) for $0.025 < f < 1$. The wavelength dependence of the dielectric constant of silica was obtained from two references; in the range of 0.2 to ~1 μm [16] and from ~1 to 50 μm [17]. Finally, the index of refraction (n_c) and extinction coefficient (k_c) of the composite was readily calculated based on the complex ε_c values [13].

Once the optical properties with respect to wavelength are obtained for all materials (including aluminium [18]) involved the calculation of the reflectivity was performed using transfer matrix formalism which is a well established method [19] and below we will shortly describe the procedure following the notation in Prentice [20].

The transfer matrix formalism assumes that forward, F, (in the direction of the incident light) and backward, B, electromagnetic waves, with amplitude E, propagate through a multilayer consisting of M-number of layers and M + 1 number of interfaces.

The refraction of the electromagnetic waves at an interface is described by relating two field amplitudes on the left (L) with two on the right side of the interface by a two dimensional tensor. Thus, we have for the refractive matrix at the m:th interface:

$$\begin{bmatrix} E_m^{LF} \\ E_m^{LB} \end{bmatrix} = \frac{1}{t_{m,m+1}} \times \begin{bmatrix} 1 & r_{m,m+1} \\ r_{m,m+1} & 1 \end{bmatrix} \times \begin{bmatrix} E_m^{RF} \\ E_m^{RB} \end{bmatrix} \quad (2)$$

where $r_{m,m+1}$ and $t_{m,m+1}$ are the Fresnel reflection and transmission coefficients, respectively, of the m:th interface. Here light is incident from the m:th layer towards the interface bounded by the m + 1:th layer. Further, each layer is associated with a matrix which describes the attenuation of right and left going waves within that layer according to:

$$\begin{bmatrix} E_m^{RF} \\ E_m^{RB} \end{bmatrix} = \begin{bmatrix} \exp(i\delta_m) & 0 \\ 0 & \exp(-i\delta_m) \end{bmatrix} \begin{bmatrix} E_{m+1}^{LF} \\ E_{m+1}^{LB} \end{bmatrix} \quad (3)$$

where $\delta_m = 2\pi N_m t_m / \lambda$ and N_m is the complex index of refraction of layer m, t_m is the thickness of layer m and λ is the wavelength. If the two dimensional tensors in Eqs. (2) and (3) above are denoted by I_m and L_m then the relationship between the incident (E_1^{LF}) and reflected (E_1^{LB}) field amplitudes and those at the second interface (m = 2, E_2^{LF} and E_2^{LB}) for light incident on the first layer is:

$$\begin{bmatrix} E_1^{LF} \\ E_1^{LB} \end{bmatrix} = I_1 \times L_1 \times \begin{bmatrix} E_2^{LF} \\ E_2^{LB} \end{bmatrix}. \quad (4)$$

Further, in order to relate E_1^{LF} and E_1^{LB} with the fields on the right side of the M + 1 interface (where layer M + 1 is the substrate or vacuum) the process is repeated M-number of times and with an additional refractive matrix for I_{M+1}:

$$\begin{bmatrix} E_1^{LF} \\ E_1^{LB} \end{bmatrix} = I_1 \times L_1 \times I_2 \ldots I_M \times L_M \times I_{M+1} \begin{bmatrix} E_{M+1}^{RF} \\ E_{M+1}^{RB} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \times \begin{bmatrix} E_{M+1}^{RF} \\ E_{M+1}^{RB} \end{bmatrix}. \quad (5)$$

Note, E_{M+1}^{RF} is the field amplitude of the transmitted wave. Further, if there is no light incident from the M + 1 layer (i.e. assuming that M + 1 layer is either vacuum or a dissipative substrate) towards the left then $E_{M+1}^{RB} = 0$.

Thus the reflection (R) is calculated by:

$$R = \frac{S_{21}}{S_{11}} \times \frac{S_{21}^{cc}}{S_{11}^{cc}} \quad (6)$$

where the superscript cc indicates the complex conjugate. It should be mentioned that the formalism is also applicable to materials described by a complex index of refraction [19] although for rough interfaces the refractive matrix is modified [21].

Finally the α, β, and η were calculated according to [22]:

$$\alpha = \frac{\int_{0.2}^{2} I_S(\lambda)[1-R(\lambda)]d\lambda}{\int_{0.2}^{2} I_S(\lambda)d\lambda} \quad (7)$$

$$\beta = \frac{\int_{2}^{50} I_P(\lambda)[1-R(\lambda)]d\lambda}{\int_{2}^{50} I_P(\lambda)d\lambda} \quad (8)$$

$$\eta = \alpha - \varepsilon\sigma T^4 / I_0 \quad (9)$$

Above I_S and I_P is the solar spectrum for air mass 1.5 [23] and black body emittance described by Planck's distribution law, respectively. Further, *T* is the absolute surface temperature (here all calculations performed for $T = 373\ K$), σ is the Stefan–Boltzmann's constant and I_0 is the solar power/unit area (i.e., the integrated solar spectrum ~900 W/m^2). Note that all the Eqs. (2)–(10) above are valid for normal incidence and emittance of electromagnetic radiation. The contribution of non-normal incidence and emittance has an effect on *R* and consequently on α, β and η. The non-normal spectral emittance values may differ significantly from those calculated/measured using the normal directional geometry, in particularly in the range of λ ~ 11 μm [24].