Numerical Study of Thermo-Chromic Properties of VO₂-Polymer Composites Coatings Applied to Building Thermal Insulation

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Abstract— Kubelka-Munk (KM) (two-flux) model was computed to solve the radiative transfer equation. The transmittance and reflectance spectra were calculated for Vanadium dioxide (VO₂) particulate film embedded in a polymer matrix. Numerical results in this work show a high similarity with experimental results reported in literature. The influence of particles concentration and thickness on the absorption coefficient K and temperature dependence of VO₂ transmittance were verified. A comparison with a four-flux model confirms the exactitude of our results. Calculations were done in the 300-2500 nm solar optical wavelength range for several particles concentration values of 1, 0.5, 0.25 and 0.1 and several thicknesses for two values of temperature 22°C and 100°C under and above (VO₂) Transition.

Keywords: Kubelka-Munk Model, Nanoparticles Concentration, Solar Modulation, VO₂ Thermo-chromic Properties.

I. INTRODUCTION

VO₂ is a thermo-chromic material which has the capacity to switch from an insulating state to a metallic state around a transition temperature of about Tc = 68°C according to F.J. Morin et al. [1]. The insulating state of VO₂ is characterized by a high transparency to solar radiations of visible and near infrared spectrum, contrarily to the metallic state in which VO₂ becomes more reflective to the infrared spectrum. A change in the crystallographic structure of VO₂ is the cause of this Insulator/Metal transition. For low temperatures T < Tc, the VO₂ crystal lattice is monoclinic, therefore, inter-atomic distances V—O and V—V are relatively big and an energy gap between electronic bands is created, H.W. Verleur et al. [2]. With this gap, VO₂ behaves as a semiconductor (SC) material according to Goodenough [3]. From an optical point of view, empty sites in the (SC) crystal structure are much important, which explains the high transparency to solar spectrum especially to near infrared wavelengths; this part of the spectrum is known as the main heat energy transporter. For high temperatures T > Tc, the VO₂ crystal structure changes to quadratic geometry (rutile), where the inter-atomic distances become much smaller, thus the energy gap disappears and the crystal behaves as a metal. Optically speaking, for these temperatures, VO₂ reflects a big part of near infrared radiations.

The ability of this material to change its optical properties depending on temperature makes of it a good candidate for applications in buildings thermal insulation. Example of these applications is energy efficient windows based on VO₂ thin films proposed by C.M. Lampert et al. [4], M. Saeli et al. [5] and Y. Gao et al. [6], this application uses the principle of radiative thermal rectification to regulate heat transfer and energy consumption in buildings. So far, the use of VO₂ in these applications is blocked by two limitations. The first one is about the high value of the transition temperature that should be near to 25°C (comfort temperature), this problem has been solved by Tungsten (W) and Fluor (F) doped VO₂ with small concentrations according to W. Burkhardt et al. [7]. The second limitation is related to the high absorption in the visible region of the solar spectrum; this phenomenon has a negative influence on the luminance of VO₂ coated windows, we can overcome it by optimizing the concentration of the absorbing particles, this solution will be treated numerically in this paper. This problem does not affect the wall applications because there is no need for high luminance and here is an invitation to more researches in this direction.
VO₂ nanoparticles are characterized by their transmittance and reflectance. Those two spectra are highly dependent on particles absorption and scattering properties. In this work, we will focus on the influence of the absorption phenomenon generated by the narrow optical band gap in VO₂ according to C.G. Granqvist et al. [8]. The numerical model used here to calculate the transmittance and the reflectance of the nanocomposite is a Two-flux model based on Kubelka-Munk (KM) theory, this model is unable to solve the particles scattering part of the radiative transfer equation because of the acute anisotropic single scattering which requires a high accuracy M.Q. Brewster et al. [9]. This type of scattering is generated by particles with small dimensions (radius r << λ) considered as a low scattering condition by K. Laaksonen et al. [10].

The two-flux model is a simple method developed by P. Kubelka et al. [11] to solve the radiative transfer equation which describes light propagation through a scattering and absorbing media. This model considers two propagation directions with descendent (transmitted) and ascendant (reflected) light flux, those two flux include absorption and scattering interactions in the illuminated media, with K and S are respectively the absorbed fraction (absorption coefficient) and the scattered fraction (scattering coefficient) of light flux.

In this work, we present a numerical characterization of VO₂ Particulate film embedded in a polymer matrix using the (KM) theory. We show the influence of the matrix thickness and the particles concentration on the absorption coefficient K, scattering is neglected because of low accuracy in the two-flux model. We make a comparison with results computed by the four-flux model and with experimental results. We calculate the transmittance for two values of temperature under and above VO₂ transition temperature 22°C and 100°C to verify numerically thermo-chromism properties.

Theory section outlines the model used for our calculations, results section presents our findings discussed and compared with recent works. The last section recapitulates results and conclusions.

II. THEORY

We consider a transparent polymer matrix with thickness containing VO₂ nanoparticles with an equivalent thickness dx = 50nm (particulate film), see fig 1. This configuration is based on some recent experimental works Y. Gao et al. [6] and I.G. Madida et al. [12], which we are here trying to verify numerically.

The incident solar radiation is divided in two fluxes i(x) and j(x) with opposite directions. When the flux j(x) passes through VO₂ particles dx, a fraction is lost (-) by absorption Kj(x) and by scattering Sj(x), yet i(x) acquire (+) Si(x) by scattering. The same reasoning is applied in the opposite direction for i(x), thus the fraction (K+S)i(x) is acquired and Sj(x) is lost. This analysis leads to the following equations system:

\[
\frac{di(x)}{dx} = (K + S)i(x) - Sj(x)
\]

\[
\frac{dj(x)}{dx} = -(K + S)j(x) + Si(x)
\]

(1)

K and S are considered respectively as the KM phenomenological coefficients of absorption and scattering according to the new KM formulation reported by P. Emmel [13]. KM theory supposes a perfectly diffuse source; therefore, K can be related to the spectral extinction \( k(\lambda, T) \) of the Beer-Lambert low. The relation between K and k(\( \lambda, T \)) is demonstrated by photometric calculations:

\[
K = 2. \ln 10. \ c \ k(\lambda, T)
\]

(2)

Where “c” is the concentration of VO₂ nanoparticles, it has the same signification as the volume fraction \( f = NV \) reported by K. Laaksonen et al. [10], it refers to the number of particles N found in a unit volume of the polymer matrix and V is the volume of a single particle.

![Fig. 1. Schematic diagram of the model used to calculate transmittance and reflectance spectra for a VO₂ particulate film embedded in a polymer matrix.](image)
The variation of this concentration has a big influence on the absorption rate; therefore a parametric study based on its variation would give optimal values of VO₂ nanoparticles concentration to overcome the high absorption localized in the visible spectrum.

Scattering coefficient S depends on the surface ratio between particles and polymer matrix, this ratio is considered as the scattering cross section which is related to the Beer-Lambert low through the total cross section formula, and thus S could be written as:

$$ S = \ln 10 \cdot c \cdot n(\lambda, T) \cdot \pi \cdot r^2 / (dx \cdot L) $$

(3)

We consider spherical VO₂ nanoparticles with radii “r”. dxL refers to the polymer surface containing VO₂ nanoparticles with refractive index “n(λ,T)”. We fixed the radius value in 5 nm to verify low scattering condition ($r \ll \lambda$); therefore, the scattering phenomenon is limited to the anisotropic single scattering with low intensity. Computing this type of low scattering requires high accuracy which is not possible with the KM method.

Our calculations are based on the matrix method represented by P. Emmel [13] as a new formulation of KM theory, thus equation (1) is written as:

$$ \frac{d(i)}{dx} = [K + S \quad -S] \frac{d(j)}{dx} $$

(4)

Solutions of this differential equation are given by the exponential of the matrix M as:

$$ M = \exp(XM) \times \left[ \begin{array}{c} i(x_0) \\ j(x_0) \end{array} \right] = [t \quad u \quad v \quad w] \times \left[ \begin{array}{c} i(x_0) \\ j(x_0) \end{array} \right] $$

(5)

With t, u, v and w are functions of the film thickness X = (x - x₀), the absorption coefficient K and the scattering coefficient S, so we can write:

$$ j(X) = \frac{v+wr_0}{t+ur_0} \cdot i(X) $$

And

$$ R = \frac{i(X)}{i(X_0)} = \frac{v+wr_0}{t+ur_0} $$

(6)

Rg is the backing reflectance of the polymer matrix at x₀ with $R_g = j(x_0)/i(x_0) = 0.1$ considered as standard glass. After the determination of Eigen values $\alpha_1 = b \cdot S$ et $\alpha_2 = -b \cdot S$ and Eigen vectors:

$$ e_1 = \left[ \begin{array}{c} 1 \\ \frac{1}{s} \end{array} \right] \text{ and } e_2 = \left[ \begin{array}{c} 1 \\ \frac{1}{s} \end{array} \right] $$

(7)

Then the exponential of the matrix M can be written:

$$ \exp(XM) = V \left[ \begin{array}{ll} \exp(\alpha_1 X) & 0 \\ 0 & \exp(\alpha_2 X) \end{array} \right] V^{-1} $$

(8)

$$ V = \left[ \begin{array}{ll} 1 & 1 \\ (a - b) & (a + b) \end{array} \right] \text{ and } V^{-1} = \frac{1}{2b} \left[ \begin{array}{ll} (a + b) & -1 \\ -(a - b) & 1 \end{array} \right] $$

(9)

With V is the transfer matrix, $b = \sqrt{a^2 - 1}$ and $a = (K + S)/S$

Transmittance and reflectance are given by:

$$ T = \frac{b}{a \sinh(bSX) + b \cosh(bSX)} $$

and

$$ R = \frac{1 - R_g(a - b \cosh(bSX))}{a + b \cosh(bSX) - R_g} $$

(10)

### III. RESULTS AND DISCUSSION

We calculated the spectral transmittance and reflectance for several nanoparticles concentrations 1, 0.5, 0.25 and 0.1. Concentration is directly related to the degree of porosity of the particulate VO₂ film, the porosity decreases as the concentration increases. For high concentration (volume fraction near to 1), nanoparticles occupy the entire volume, thus, we obtain low porosity and high absorbance because of the high number of absorbing particles. As a result, the transmittance drop very clearly in the visible region, see (fig 2-a, 2-b). In the case of low concentration, porosity becomes more important and absorbance decreases, therefore, the transmittance increases considerably in the majority of the spectrum, see (fig 2-c, 2-d).

Our numerical results are in good agreement with experimental findings obtained by Gao et al. [6] for VO₂ particulate film deposited by polymer-assisted sol-gel process, especially between transmittance at c = 0.5 (fig 2-b) and transmittance of simples annealed at high temperatures for a long time. Annealing changes the particles ratio between the polymer and VO₂ because of polymer evaporation, which is equivalent to increasing the nanoparticles concentration.
Comparing our results to those calculated by K. Laaksonen et al. [10] using the four-flux method, we noticed a huge difference in transmittance for metallic state particularly in the infrared part of the spectrum with an increase in transmittance after a minimum at 1200 nm for the four-flux method, while in our results, the metallic state transmittance continue decreasing in infrared. This can be explained in two points. In one hand, there is a lack of accuracy of the two-flux method related to scattering phenomena produced by particles with small dimensions (r \ll \lambda). In the other hand, a morphological difference exists between particulate films simulated in this work and nanoparticles studied in [10].

Another aspect that we can notice from our results is that the optical modulation $\Delta T$ which occurs at the transition between semiconductor and metallic state [14-18] depends on VO$_2$ concentration. $\Delta T$ For the concentration $c = 0.1$ at $\lambda = 2\mu$m is about 37% (fig 2-d) while for $c = 0.5$ at the same wavelength the modulation is about 70% (fig 2-b). This dependence was found experimentally by I.G. Madida et al. [12] for a submicronic VO$_2$-PVP composite by modifying the relative mass ratio $C_{VO_2/PVP}$ which is the same as our “c” value, they reported that the higher is the relative mass ratio, the larger is the optical modulation and this is what we found numerically.
In figure 3, we tried to see the impact of thickness on the thermo-chromic properties of the VO$_2$ particulate film. We fixed the concentration at a value of 0.2 and calculate the transmittance at 22°C and 100°C for thicknesses of 43 nm, 102 nm, 215 and 428 nm. We found that thickness has the same influence as concentration. The transmittance decreases as the thickness increases because the ratio VO$_2$/Polymer tends to 1, so the absorption increases. We found also that the optical modulation across the VO$_2$ transition is highly dependent to thickness. For example, a 102 nm film exhibits a transmittance change of 72% at 2µm whereas a 43nm film shows a change of 52% at the same wavelength (see figure 3). The same behavior was noticed experimentally by Gao et al. [6] for VO$_2$ particulate films. The impact of thickness can be used as an adjustment tool for the optical modulation.

Refractive index $n(\lambda,T)$ and extinction coefficient $k(\lambda,T)$ employed in this study were measured at 22°C and 100°C by N.R. Mlyuka et al [20]. We were authorized to use this data by Mr. C.G. Granqvist.

**IV. CONCLUSION**

In the present work, we solved the radiative transfer equation in aVO$_2$ particulate film embedded in a polymer matrix using a two-flux method based on Kubelka-Munk theory. Transmittance and reflectance were calculated for several values of VO$_2$ particles concentration and thicknesses. In this study, we verified numerically the high dependence of absorption phenomena to particles concentration and thickness. We noticed that our results are in good agreement with experimental studies realized in the same context. We mentioned the difference between a two-flux and a four flux method regarding the scattering issue. We validated the fact that optical modulation at VO$_2$ transition depends also on the particles concentration and thickness. VO$_2$ coatings are considered as a reliable solution for buildings thermal insulation, it means that in winter, VO$_2$ allows having thermal gains inside buildings by letting the solar radiations enter and vice versa, in summer, VO$_2$ blocks the radiative heat transfer.
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