Calculation of infrared properties of low emissivity coatings containing metallic flake pigments

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The infrared emissivity of low emissivity coating can be significantly reduced by adding high content concentrations of parallel distributed metallic flake pigment. However, the infrared emissivity is very difficult to calculate by the existing theory models, such as the light scattering theory and traditional Kubelka-Munk radiative transfer model, because of shape and distribution anisotropy of flake pigments. Thus, the low emissivity coating is assumed to be the superposition structure of homogeneous layers and metallic flakes are approximately uniform and parallel arrangement in each layer. Based on geometric optics theory and Kubelka's layer model, considering multiple reflection, transmission and absorption of infrared radiation among different layers, the theoretical model is established to calculate the coating emissivity. The facts of binder, pigment concentration and thickness are also systematic discussed. The result shows that the law of influence on infrared emissivity can be correctly simulated by this theoretical model. Transparent binder, high volume concentration of thin flake pigment can facilitate to reduce infrared emissivity. Moreover, this model offers the possibility of predicting the infrared optical properties of coatings by their optical constants.

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Low infrared emissivity coatings have received extensive attention as the important energy-saving and infrared camouflage material in both civil and military purposes due to its high performance, simple operation, and cheap cost[1,2]. In order to achieve optimal performance, the infrared emissivity of the coating must be as low as possible[1]. Nearly transparent polymeric binder and high infrared reflectance pigment are two key factors to obtain low infrared emissivity[1]. However, because of high emissivity of conventional organic binder, the average baseline of infrared spectrum over the entire infrared spectral region mainly changed by metal pigment[3] such as Ag and Al flake pigment, which size, shape, and distribution significantly affect infrared emissivity[4,5]. It is very important that building a suitable model to reflect the impact of these factors and calculate the infrared emissivity of the coating.

Infrared radiation property of low emissivity coating with spherical pigment has been extensively researched, and various mathematic models have been established[6−9]. Because spherical pigment is the isotropic scatterer, the emissivity/reflectivity of this coating should be calculated by Kubelka-Munk theory[10,11] and Mie theory[9,12]. This mathematical model of coating emissivity also can be expanded to ellipsoid or cylindrical pigment particles system[6−12].

Compared to the conventional spherical metal pigment, metallic flake pigments have larger effective surface area to reflect infrared radiation back into space immediately , which will further reduce the emissivity of the coating[1]. In addition, flake pigment is anisotropic scatterer. It is too complex to discuss anisotropic scattering and the angle-dependent optical effect of flake pigment by Mie theory[9]. Recently, it is reported that there are some attempts to establish the calculate models of coating infrared emissivity by other theories, such as rough-surface model[3], two-layer structure model[13], and ray scattering model based on the topographic map of the coating[14]. In spite of the fact, there is still not simple and suitable mathematical model which can be used to accurately predict the infrared emissivity of the inhomogeneous coating with flake pigment.

Therefore, the purpose of this letter is to establish a suitable mathematical model of inhomogeneous coating system with metallic flake pigment that can accurately predict infrared emissivity. First of all, the distribution and orientation of flake pigments inside the coating is analyzed. Then, inhomogeneous coating is equivalent to a superposition structure consisting of multilayers. And based on geometrical optics theory and Kubelka's layer model, the emissivity prediction model is established. At last, the influence of factors, such as binder, aluminum concentration, coating thickness, and pigment thickness on coating emissivity, is systematically discussed.

The discrete two-flux model was introduced by Kubelka[15]. Kubelka's layer model describes the multiple reflections and transmissions of light among various superposed diffusing layers. Emissivity of the multilayer structure can be obtained from its optical constants[16].

In previous report[17], it had been found that orientation of flake pigment could be controlled by additive and painting process, which was uniformly distributed in the coating and approximately parallel to the coating surface (see Fig. 1).

Therefore, the low emissivity coating can be assumed to be multistory structure composed by thin homogeneous layers (see Fig. 2). X_p is the volume content of flake pigment relative to the binder (X_p=1 at 100% solid content of pigments), and d is the thickness of flake aluminum pigments. The relationship between d and coating thick-

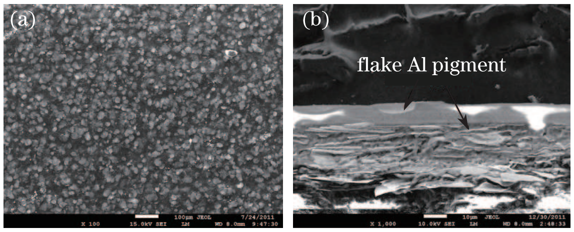

Fig. 1. (a) Surface and (b) cross section scanning electron microscopy (SEM) images of the low-emissivity coating (pigment size: 20 μm).

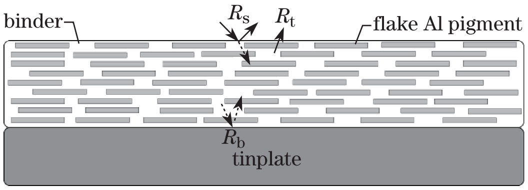

Fig. 2. Schematic diagram of low-emissivity coating.

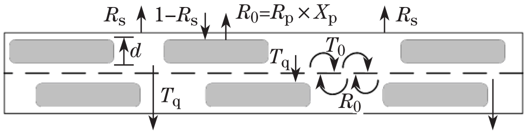

Fig. 3. Reflection-transmission of light with superposed symmetrical layers.

ness h is $n = h/d$.

In order to simplify theory model, following hypotheses are proposed: 1) flake pigment is completely homogeneous and parallel arrangement along the surface direction of the coating; 2) high reflectance aluminum pigment and substrate is considered of infrared weak absorption and opaque materials. Thus, the influence of infrared absorption and transmission should be ignored; 3) flake aluminum pigments have the same particle size and thickness d; 4) the surface of coating, aluminum pigment, and tinplate is perfectly smooth.

As shown in Fig. 3, in a monolayer, a part of the infrared radiation was reflected by flake aluminum pigments and the remainder radiation could reach to the next layer across resin gaps. Thus, The monolayer's reflectance and transmittance are relevant for the pigment thickness d, the binder–air interface reflectance $R_{\mathtt{s}}$, the resin-aluminum interface reflectance $R_{\mathtt{p}}$, and the resin absorption coefficient α. Figure 3 shows the reflection and transmission scheme of the infrared beam when it impinged the coating surface at a normal incident angle. The monolayer's reflectance R_0 and transmittance $T_{\mathtt{q}}$ are

$$R_0 = R_{\mathtt{p}} X_{\mathtt{p}}, \tag{1}$$

$$T_{\mathtt{q}} = (1 - R_{\mathtt{p}} X_{\mathtt{p}}) e^{-\alpha d}. \tag{2}$$

$R_{\mathtt{p}}$ can be solved by the Fresnel formula[18]

$$R_{\mathtt{p}} = (\frac{n_1 - n_2}{n_1 + n_2})^2, \tag{3}$$

where n_1 and n_2 are the refractive indexes of aluminum and resin, respectively. The absorption coefficient α[18] of the coating is related to the extinction coefficient k of the resin by

$$\alpha = \frac{4\pi\kappa}{\lambda}. \tag{4}$$

When multilayers are superposed together, their global reflectance and transmittance can be computed according to Kubelka's layer model[15] and expressed as functions of the individual layer reflectance and transmittances[16]. First of all, a 'bilayer' structure, which is composed by two layers with the same R_0 and $T_{\mathtt{q}}$, should be discussed. Figure 3 also shows the multiple reflection–transmission process of infrared radiation between two layers.

Based on the Kubelka's layer model and taking into account multiple reflections and transmissions of infrared radiation, a geometric series expressing of the bilayer's global reflectance and transmittance is obtained:

$$\begin{aligned} R_2 &= R_0 + T_{\mathtt{q}} R_0 T_{\mathtt{q}} + T_{\mathtt{q}} R_0^3 T_{\mathtt{q}} + \cdots + T_{\mathtt{q}} R_0^n T_{\mathtt{q}} \\ &= R_0 + T_{\mathtt{q}}^2 R_0 \frac{1}{1 - R_0^2}, \end{aligned} \tag{5}$$

$$T_2 = T_{\mathtt{q}}^2 + T_{\mathtt{q}}^2 R_0^2 + T_{\mathtt{q}}^2 R_0^4 + \cdots + T_{\mathtt{q}}^2 R_0^n = T_{\mathtt{q}}^2 \frac{1}{1 - R_0^2}. \tag{6}$$

To facilitate its iterative operation, each layer's optical property may be represented by the layering matrix[13], where the reflectance and transmittance is arranged as

$$\mathbf{M_1} = \begin{bmatrix} 1 & -R_1 & 0 \\ R_1 & A_1 & 0 \\ 0 & 0 & T_1 \end{bmatrix}, \tag{7}$$

where $A_1 = T_1^2 - R_1^2$. A superposition of layers is equaled to the multiplication of their layering matrices[16]. Therefore, as shown in Fig. 3, its layer layering matrix $\mathbf{M_2}$ of the bilayer is

$$\mathbf{M_2} = \frac{1}{1 - R_1^2} \mathbf{M_1}^2 = \begin{bmatrix} 1 & -R_2 & 0 \\ R_2 & A_2 & 0 \\ 0 & 0 & T_2 \end{bmatrix}. \tag{8}$$

It can be generalized to the superposition of n layers. Its global reflectance and transmittance can be obtained:

$$R_{\mathtt{t}} = \mathbf{M}_n(2,1)/\mathbf{M}_n(1,1), \tag{9}$$

$$T_{\mathtt{t}} = \mathbf{M}_n(3,3)/\mathbf{M}_n(1,1). \tag{10}$$

In order to calculate the reflectance of the low emissivity coating, it is also necessary to take into account the multiple reflection–transmission of infrared radiation between air-coating and coating-substrate interfaces. Then, the global reflectance R_∞ of the coating is

$$R_\infty = R_{\mathtt{s}} + (1 - R_{\mathtt{s}})^2 R_{\mathtt{t}} + (1 - R_{\mathtt{s}})^2 T_{\mathtt{t}}^2 R_{\mathtt{b}} \frac{1}{1 - R_{\mathtt{b}} R_{\mathtt{t}}}, \tag{11}$$

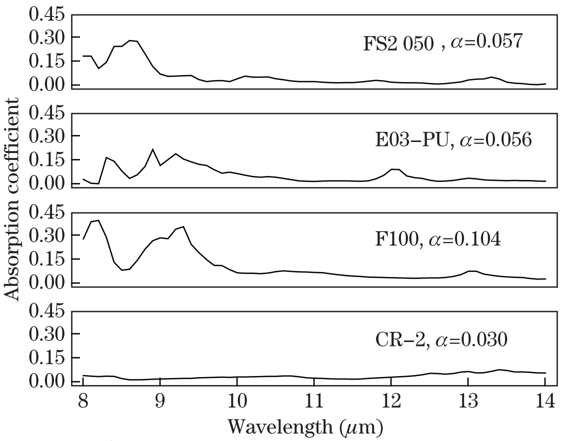

Fig. 4. Absorption coefficient of various binders.

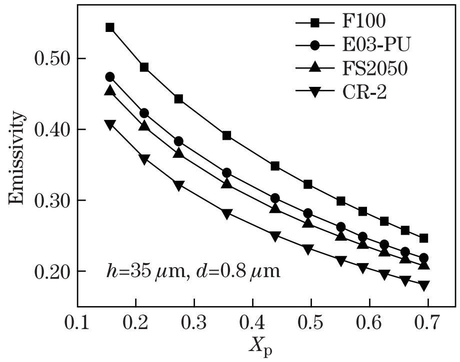

Fig. 5. Infrared emissivity of the coatings containing various binders at different pigment volume contents X_p.

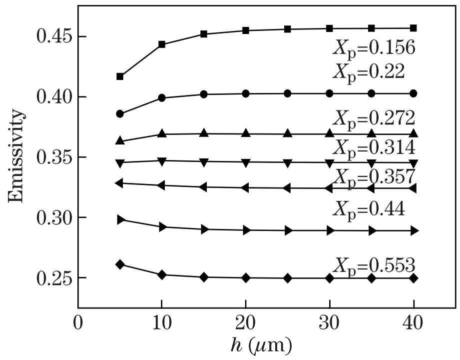

Fig. 6. Infrared emissivity of the coatings containing various pigment content at different coating thicknesses (d=0.8 μm).

where R_b is the reflectivity of resin-tinplate interface.

In the low-emissivity coating, the factors of binder, pigment content, coating thickness, and flake pigment morphology, etc., are mainly effect the infrared emissivity of coating[4,5]. Therefore, in this work, the influences of these parameters are systematically investigated, respectively.

Binder is one of the key factors, because some parameters, such as R_s, R_0, T_q, and α, will change with the optical property of binder. Thus, four kind of polymer-based binders (acrylic resin FS2050, epoxy-Polyurethane E03-PU, fluorocarbon resin F100, and chlorinated rubber CR-2) are chosen. In Fig. 4, it can be seen that the fluorocarbon resin F100 has highest infrared absorption coefficient in the waveband of 8–14 μm. And the infrared transmittance of chlorinated rubber CR-2 is optimal due to its simpler molecules structure.

As shown in Fig. 5, the coating prepared by chlorinated rubber has lowest emissivity. The fluorocarbon resin is unsuitable for low emissivity coating due to its high infrared absorption.

Figure 5 also shows that the emissivity of all samples gradually decreases with increasing the volume content X_p. The increase in Al pigment content could increase the amount of the pigment particles in the coating, resulting in the closer parking of the particles, which then leads to increase reflectivity R_0 and decrease transmittance T_q. Thus, more infrared radiation can be reflected by the coating. Yu *et al.*[19] also researched the relationship between content of metal pigment and infrared emissivity of coatings. It is reported that the emissivity decreases significantly with increasing pigment concentration. The changing rule coincides well with the result in Fig. 4. This proves that this theoretical model can rightly reflect the effect of binder on infrared emissivity.

However, it must be noted that the concentration of flake pigment cannot be unlimitedly increased. It must be controlled in the reasonable scope. If pigment content exceeds the critical pigment volume concentration (X_{CPVC}), mechanical properties of the coating will deteriorate quickly[1].

In previous reports[19], it shows that the coating thickness h has a large effect on emissivity due to the penetrate thickness of infrared radiation in the coating. Figure 6 shows the relationship between the coating thickness, pigment concentration and infrared emissivity of FS2050/Al coatings. As shown in Fig. 6, the coating thickness also has obvious effect on infrared emissivity. It can be seen that the tendency of emissivity has significant difference in various coatings. The emissivity increases with increasing the coating thickness when X_p is greater than 31.36%. Conversely, it shows the opposite change of the emissivity at low pigment content (X_p <31.36%). The emissivity gradually reaches to a stable value when the coating thicknesses exceed 15 μm.

The reason could be attributed to the effect of high reflectance substrate. When the thickness h is relatively low, the coating has high transmittance T_t, and the infrared radiation can penetrate the thin coatings. Thus the emissivity could be influenced by the substrate. With increasing of thickness h, T_t is decreased gradually (see Fig. 7), which also reduce the influence of substrate.

In addition, as shown in Fig. 7, the layers' global reflectance R_t and transmittance T_t is closely related to X_p. At the high pigment content, R_t should be improved. If the layer's reflectance R_t is larger than the substrate reflectance, the coating emissivity will reduce with increasing the thickness h.

As shown in Fig. 8, the coating emissivity can be strongly affected by the thickness d of flake aluminum particles at the various coating thickness h. The coating emissivity obviously increases with increasing aluminum flake thickness d. It could be attributed to decrease of the monolayer's transmittance T_q caused by increasing pigment thickness (see Eq. (2)). In addition, the relationship between coating thickness and emissivity shows remarkable differences due to various flake thicknesses d.

At low d (i.e., d=0.2 μm), the monolayer is very thin. If the infrared radiation only crossed a short thickness, most of the radiation can be reflected through the coat ing surface. On the contrary, large flake thickness d leads high infrared absorption of monolayer and decreases the number of multilayers. Thus, the thin flake pigment is more helpful to reduce the skin depth and infrared absorption.

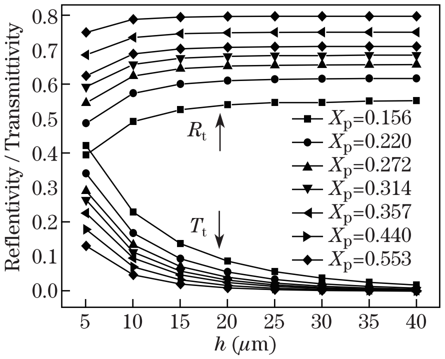

Fig. 7. Global reflectance and transmittance of the coatings containing various pigment content at different coating thicknesses (d=0.8 μm).

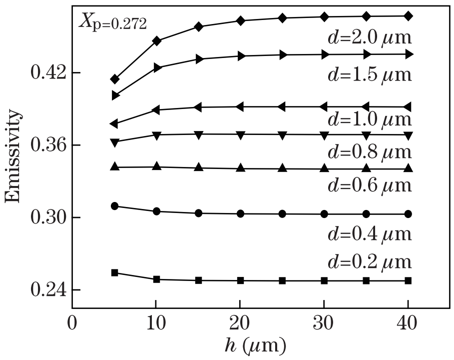

Fig. 8. Infrared emissivity of the coatings at different flake thicknesses.

In conclusion, based on geometric optics and multilayer film theory, the theoretical model is established to calculate the coating emissivity. And various parameters, such as binder, pigment concentration and thickness are systematic discussed. The result shows that the coating containing transparent binder, high volume content of thin flake pigment helps to obtain low infrared emissivity. This changing rule reflected by the theoretical results is coincided well with the measuring data reported by the references. Moreover, this model makes it possible to adjust these factors to obtain the required properties of the coating. It is hoped that this work will be useful for designing an actual coating.

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