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Optical and magnetic properties of Al/Fe_3O_4 core–shell low infrared emissivity pigments

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ABSTRACT

A core–shell Al/Fe_3O_4 magnetic composite pigment has been prepared by solvothermal method in order to obtain low infrared emissivity pigment with low lightness and visible reflectance. The influence of the shell layer thickness, surface roughness and radiation wavelength on spectral reflectivity of Al/Fe_3O_4 composite pigment is systematically researched by geometric optics theory and rough surface theory. The Al/Fe_3O_4 composite pigment with low visible reflectance and high infrared reflectance can be designed by thin thickness and high surface roughness of the shell layer. Then, Al/Fe_3O_4 composite pigments with different covering content of Fe_3O_4 are prepared by adjusting the molar ratio of Fe^{3+}:Al. The phase structure, surface morphology, reflectance spectra and magnetic hysteresis loop of samples are characterized by XRD, FE-SEM, UV/VIS/NIR spectroscopy, Fourier transform infrared spectrometer and VSM. The result shows that the surface covering content rises with the increase of Fe^{3+}:Al, which significantly reduces the VIS reflectance and lightness of flake Al pigment but only slightly increases the infrared emissivity at low molar ratio of Fe^{3+}:Al. There are only a few of the surface coated with a thin Fe_3O_4 layer when the molar ratio of Fe^{3+}:Al is 0.075:1, but the surface roughness of flake Al pigment significantly increases. The lightness L^* and visual light reflectivity can be decreased by 12.8 and 0.34 as compared to the uncoated flake Al pigment, but the infrared emissivity is only increased by 0.04. The saturation magnetization value of the composite pigment is 11.9 emu/g, which could help improve the radar stealthy performance. Therefore, these Al/Fe_3O_4 magnetic composite pigments can be used as a novel low infrared emissivity pigment to improve the stealthy performance of the coating in the visual, IR and Radar wavebands.

1. Introduction

Flake aluminum pigment is the most common low infrared emissivity pigment due to its low emissivity, cheap cost and easy directional arrangement [1–3], which is widely used to prepare the low infrared emissivity coating (Low-E coating), such as energy conservation coating and military camouflage coating [1,4]. As the infrared camouflage coating, the infrared emissivity of the coating in the range of infrared atmospheric window (8–14 μm) should be kept as low as possible [1,2]. In order to reduce the infrared emissivity, high concentrations of flake aluminum pigments must be added into the coating, which also leads to high lightness (L^*) and radar reflectivity of the coating due to high reflectivity of metallic aluminum pigment in the VIS, NIR, IR and Radar wavebands [5]. However, the lightness and VIS reflectance of Low-E coating should be as low as possible, either as colorized energy-saving coating or VIS/IR/Radar multi-functional camouflage coating [5]. In traditional technologies, high concentrations of colored pigments are added to adjust the color and reduce the lightness and VIS reflectance [6]. However, most of the colored pigments are high infrared absorbing material, which can be sure to increase the infrared emissivity of the coating [6]. In addition, high concentrations of flake aluminum pigments also increase the coating's permittivity and radar reflectance [1]. Thus, it is very difficult to prepare the Low-E coating with low lightness, low infrared emissivity and low radar reflectance simultaneously.

In the past few years, most of the researches have been focused on improving the corrosion resistance of metal pigment [7–8] and gain some additional optic [9–11], electrical [12] and magnetic [13,14] characteristics by the cover treatment method. There have been few reports on the low emissivity pigment with low lightness and a certain magnetism, which can be specifically used in Low-E coating. L. Yuan has reported a composite pigment through coating Cr_2O_3 on the surface of flake aluminum powders [5]. Compared with uncoated flake aluminum powders, its visible light reflectance and lightness (L^*) drops 50% and 15, respectively, while the infrared reflectance in the range of 8–14 μm waveband reduces less than

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10% [5]. This Al/Cr_2O_3 composite pigment has good stealthy performance in VIS and IR wavebands. However, it has no contribution on improving stealth compatibility in radar waveband.

The cover treatment is an important surface modified method. If a shell layer with a certain thickness is uniformly covered on the surface of the core, it is possible to prepare a core/shell material that has the properties of the core and shell materials [15–18]. Magnetite (Fe_3O_4) is a kind of black magnetic pigment. It has attracted more attention for their potential applications in diverse fields including coloring pigment and microwave absorbing material [19–21]. Liu has prepared Carbonyls iron powder (CIPS)/Fe_3O_4 core/shell composites by a simple hydrothermal, which microwave absorption properties can be enhanced because of the ferromagnetic Fe_3O_4 shell layer [14]. A. Amarjargal has reported a kind of core–shell Ag/Fe_3O_4 nanocomposites, in which high catalytic degradation, bacterial inactivation and enhanced magnetism can be achieved simultaneously by the special core–shell structure [22]. We also reported a core–shell composite magnetic pigment with coating Fe_3O_4 on the surface of flake aluminum powder by the cover treatment [23]. When the radiation reaches the surface of composite pigment, a portion is absorbed by the Fe_3O_4 shell layer and another portion is scattered by the rough surface. The spectral reflectivity of core–shell Al/Fe_3O_4 pigment is strongly affected by the thickness and surface roughness of the shell layer. Furthermore, the absorption and scattering change with different wavelength of radiation. Thus, although Fe_3O_4 is a kind of high infrared absorption material [21], it is possible to greatly restrain the lightness and VIS reflectance but slightly increase the infrared emissivity when an optimized Fe_3O_4 layer is covered on the surface of Al pigment. This magnetic pigment also can loss radar wave to some extent [20]. The dark magnetic composite pigment can be used to be an excellent low infrared emissivity pigment with radar absorption and low lightness.

In this paper, firstly, the influence of thickness and surface roughness of Fe_3O_4 shell layer on the spectral reflectivity in the range of 0.4–14 μm wavebands has been studied according to the geometric optics theory and rough surface theory. Then, the core–shell Al/Fe_3O_4 composite pigment with different covering contents of Fe_3O_4 was prepared by adjusting the molar ratio of Fe^{3+}:Al. The influence on optical reflectivity, visible light lightness and magnetic properties was systematically investigated. According to the optimized molar ratio of Fe^{3+}:Al, the magnetic composite pigment with low lightness, low visible light reflectivity and low infrared emissivity was prepared.

2. Experimental details

2.1. Materials

Ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), ammonia water (NH_4OH), SDBS (sodium dodecyl benzene sulfonate), ethanol, and EDA (ethylenediamine) were all obtained from Sinpharm Chemical Reagent Co., Ltd. All chemicals were A.R. grade.

2.2. Synthesis of Al/Fe_3O_4 composite material

The core–shell Al/Fe_3O_4 composite pigment was prepared by the solvothermal method using ethylenediamine as the reaction solvent. Firstly, according to the recipe (Table 1), $Fe(NO_3)_3{\cdot}9H_2O$, SDBS and flake aluminum were added into ethanol solution, and dispersed by ultrasonic vibration. A NH_4OH–ethanol solution (0.27 M NH_4OH) was added into the suspension under magnetic stirring at 60 °C. After the precipitin reaction, the products were separated by centrifugation, washed with ethanol for several times and then dried at 80 °C for 4 h. The golden precursor then formed. Next, the precursor was added into a closed Teflon-lined stainless steel chamber with a capacity of 100 ml and containing an 80 ml ethylenediamine solvent. Al/Fe_3O_4 composite powders were prepared by the solvothermal reaction at 250 °C for 24 h. After that, the Al/Fe_3O_4 composite pigments were obtained by centrifugation, cleaning and drying.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD) (SHIMADZU, XRD-7000 with CuKa radiation) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F). The VIS/NIR reflection spectrum (380–2500 nm) was measured by UV/VIS/NIR spectrophotometer (Perkin–Elmer, Lambda750). And the CIELAB color data (L^*, a^* and b^*) was calculated from the VIS reflection spectrum by Color CIE software (Perkin–Elmer, CIE D65 photo source, 10° observation angle, the calculated spectrum range: 400–700 nm). Infrared reflectance spectrum was measured by a Fourier transform infrared spectrometer (BRUKER, Tensor27) with integrating sphere attachment. Magnetization measurement was obtained by vibrating sample magnetometer (Versalab, Qutumn Desig). In this work, all measurements were done at ambient temperature.

3. Theory

The structure of core–shell composite pigment is illustrated in Fig. 1. A homogeneous Fe_3O_4 layer is coated on the surface of the flake Al powder with thickness d and absorptivity α for the Fe_3O_4 layer, with reflectance R_f for the air–Fe_3O_4 interface, and with reflectance R_{Al} for the Fe_3O_4–Al interface. Assuming that the surfaces of aluminum and Fe_3O_4 layer are completely smooth, the multiple reflection–transmission process of light within the core–shell structure is showed in Fig. 1(a). Considering a light normally incidences on the mirror surface of the Fe_3O_4 layer, a portion of light is reflected back into the air, and the other portion is refracted with partially absorbing by the Fe_3O_4 layer. Once reaching the Fe_3O_4–Al interface, the remained portion of light is reflected back into the Fe_3O_4 layer. Then a portion can be returned into the air after the absorption and reflection again. This multiple reflection–transmission process will continue until the light is depleted completely.

Summing the different fractions of light emerging at the upper side, we obtain a geometric series expressing the global specular reflectance [24]:

$$R_{th} = R_f + (1 - R_f)^2 \cdot R_{Al} \cdot e^{-2ad} + (1 - R_f)^2 \cdot R_{Al}^2 \cdot e^{-4ad} + \cdots \quad (1)$$

Whose sum is

$$R_{th} = R_f + \frac{(1 - R_f)^2 \cdot R_{Al} \cdot e^{-2ad}}{1 - R_f \cdot R_{Al} \cdot e^{-2ad}} \quad (2)$$

where R_f, R_{Al} and α can be calculated from the complex refractive index of Fe_3O_4 and Al according to the Fresnel's equation [25]. Complex refractive indexes of Fe_3O_4 and Al [21,26–27] are represented by $n_1 + ik_1$ and $n_2 + ik_2$, respectively.

$$R_f = \frac{(n_1 - 1)^2 + k_1^2}{(n_1 + 1)^2 + k_1^2} \quad (3)$$

$$R_{Al} = \frac{(n_1 - n_2)^2 + (k_1 - k_2)^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2} \quad (4)$$

$$\alpha = -4\pi k_1/\lambda \quad (5)$$