Galvanic displacement synthesis of Al/Ni core−shell pigments and their low infrared emissivity application

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ABSTRACT

We have successfully developed a magnetic Al/Ni core−shell pigment via a galvanic displacement reaction to obtain low infrared emissivity pigment with low lightness and visible light reflectance. Al/Ni core−shell particles were prepared via a simple one-step synthetic method where Ni was deposited onto the Al surface at the expense of Al atoms. The influence of pH and the amount of NH_4F complexing agent on phase structure, surface morphology, optical and magnetic properties were studied systematically. The neutral condition and high concentration of NH_4F forms smooth, flat, uniform and dense Ni shell on the surface of flake Al particles, which can significantly reduce the lightness and visible light reflectance but slightly increase the infrared emissivity. When the core−shell pigments are prepared in neutral pH solution at $NH_4F = 11.2$ g/L, the lightness (L^*) and visual light reflectivity can be reduced by 12.6 and 0.46, respectively versus uncoated flake Al pigments, but the infrared emissivity is only increased by 0.02. The color changes from brilliant silver to gray black and the saturation magnetization value is 6.59 emu/g. Therefore, these Al/Ni magnetic composite pigments can be used as a novel low infrared emissivity pigment to improve the multispectral stealth performance of low-E coatings in the visual, IR and Radar wavebands.

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1. Introduction

Flaky aluminum powders are important low emissivity (Low-E) pigments that are widely used in infrared stealth coatings (Low-E coating) due to their high infrared reflectance, cheap cost, and easy directional arrangement [1−4]. It is well known that the optical, infrared and radar stealth characters of low-E coatings influence and restrict each other [1,5]. To reduce the infrared emissivity, the high concentrations of large flakey aluminum pigments must be added to the low-E coating [1−3]. This also leads to high lightness (L^*) and strong radar reflection due to the high reflectivity of flake Al pigments across the entire Visible-IR-Radar wavebands [1]. Thus, a serious obstacle to the development of a high-performance Low-E coating, which can satisfy the demands of both optics and radar stealth, is the difficulty in finding a novel low-E pigment with low lightness and radar reflectance while keeping high infrared reflectance.

The cover treatment is an important surface modified method [6−8]. When a dark thin shell layer is uniformly covered on the surface of the flake Al powder, it has excellent extinction effect for visible light, but only slightly affects the infrared reflectance [9]. For this purpose, the binary and ternary core−shell composite materials have been investigated in the past research such as Al/Cr_2O_3, Al/Fe_3O_4, $SiO_2/Ag/TiO_2$, etc [10−12]. However, the optical performance of core−shell materials is strongly influenced by the shell material and preparation method. The traditional metal oxide shell layer is usually deposited with wet chemical method, such as chemical precipitation, sol−gel method and electrochemical synthesis [10−15]. Although this can potentially offer low lightness and visible light reflectance, the infrared emissivity is significantly increased by the oxide shell because of its high infrared absorbance. In addition, the cladding rate is relatively low due to the homogeneous nucleation [10,11]. There are many oxide particles sticking to the surface of flake Al pigment, which dramatically increased the infrared absorption.

To overcome this deficiency, the galvanic displacement method is used to prepare bimetallic Al/Ni core−shell powders. On one hand, the infrared reflectance of metal Ni is higher than that of the

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metal oxide. On the other hand, the galvanic displacement reaction is a special chemical plating method that offers controllability, high cladding rates, low costs, and batch manufacturing [16–19]. Because the standard electrode potential of aluminum is lower than nickel, Ni^{2+} can be replaced by aluminum at the solid–liquid interface only if Ni^{2+} comes into contact with the Al substrate [18,19]. This ensures that the generated metal Ni is preferably deposited on the surface of the Al substrate rather than forming new Ni particles. Thus, the cladding rate and quality can be significantly improved.

However, the galvanic displacement process is significantly affected by the reaction condition [16–21]. On one hand, high quality Al/Ni core–shell pigment can only be prepared in weakly acidic and neutral environments [18,19]. On the other hand, the displacement reaction can occur only if the surface Al_2O_3 oxide layer is removed. To remove the oxide layer in the weakly acidic or neutral environment, F^- is introduced into the reaction system as a coordinating ion of Al^{3+} to form a stable complex $[AlF_6]^{3-}$ [18,19]. Due to the complex effects between F^- and Al^{3+}, the Al_2O_3 layer is dissolved mildly and vanished eventually. However, the pH value and concentration of F^- is closely related to the deposition and growth of Ni shell, which will certainly affect the optical performance of the Al/Ni core–shell pigment.

In this study, the galvanic displacement method is used to prepare bimetallic core–shell Al/Ni magnetic pigments to develop innovative low emissivity pigments. The influence of pH and the concentration of F^- on phase structure, morphology, optical, and magnetic properties were systematically investigated.

2. Materials and methods

2.1. Materials

Nickel chloride ($NiCl_2$), ammonium fluoride (NH_4F), SDBS (sodium dodecyl benzene sulfonate), PEG1000 (polyethylene glycol) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were A.R. grade.

2.2. Synthesis of Al/Ni composite material

In a typical synthesis, 1 g of flake Al powder was added to 50 ml of ethanol solution in a 250 ml conical flask and dispersed by ultrasonic vibration. The 0.21 g SDBS and 0.2 g PEG1000 were dissolved into 50 ml of NaAc-HAc buffer solution (pH = 5.5, 6.0 or 6.4) or distilled water (pH = 7.2). This was injected into the conical flask. After stirring for 30 min, 50 ml of nickel chloride solution (17.6 g/L) was added dropwise. Half an hour later, 50 ml of ammonium fluoride solution (0–15 g/L) was also added dropwise under magnetic stirring (350 r/min) at 40 °C. The color of the powders varied from brilliant silver to dark gray after a few minutes. After another hour, the products were separated by centrifugation and washed with ethanol and distilled water several times and then dried at 80 °C for 12 h. This yielded the black-gray Al/Ni core–shell pigments.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD-7000 with CuKa radiation, Shimadzu) and field emission scanning electron microscopy (JSM-7600F, JEOL). Thermogravimetry and differential scanning calorimetry (TG–DSC) analysis was performed using a NETZSCH STA 449F3 instrument under O_2 atmosphere from 30 to 850 °C at 20 °C/min. The specific surface area was measured via BET specific surface area analyzer (ASAP 2020HD88, Micromeritics Instrument Ltd.). The VIS/NIR reflection spectrum

(380–2500 nm) was measured with a UV/VIS/NIR spectrophotometer (Lambda 750, Perkin–Elmer). The CIE LAB color data (L^*, a^*, and b^*) were calculated from the visible light reflection spectrum by Color CIE software (Perkin–Elmer, CIE D65 photo source, and 10° observation angle; the calculated spectrum range was 400–700 nm). The infrared reflectance spectrum was measured with a Fourier transform infrared spectrometer (Tensor27, BRUKER) with an integrating sphere attachment. The infrared emissivity in the range of 8–14 μm was calculated via the following equation [22]:

$$\varepsilon = \frac{\int (1 - R(\lambda)) M_{bb}(\lambda, T) d\lambda}{\int M_{bb}(\lambda, T) d\lambda} \tag{1}$$

The Planckian function $M_{bb}(\lambda,T)$ gives the intensity emitted by a black body at a certain wavelength λ and temperature T. The magnetization measurement was obtained with a vibration sample magnetometer (VSM-Versalab, Quantum Design).

3. Results and discussion

3.1. The phase structure of the samples

Fig. 1 presents XRD patterns of the Al/Ni products obtained at different pH conditions. Versus uncoated Al powders, the XRD pattern shows some extra characteristic diffraction peaks at 2θ values of 52° and 76.5°. These are indexed as the cubic phase Ni (200) and (220) crystal planes, respectively. Based on XRD data, there are only the Al (JCPDS, file No. 04-0787) and Ni (JCPDS, file No. 04-0850) phases in the product rather than the Al–Ni alloy phase. This illustrates that Ni^{2+} ions are successfully replaced by Al substances via the galvanic displacement method without any other reaction between the Al core and Ni shell. In addition, the XRD diffraction peaks corresponding to Ni (200) crystal planes gradually weaken and widen with decreasing pH values. This indicates that the strong acidic solution is not beneficial for the formation of the Ni shell.

Fig. 2 shows the XRD patterns of the Al/Ni products prepared at different concentrations of NH_4F. As shown in Fig. 2, there are only minor Ni diffraction peaks at low concentrations of NH_4F. This proves that it is very difficult to perform the displacement reaction unless the concentration of F^- is over 3.8 g/L. Fig. 2 also shows that the intensity of Ni peaks gradually strengthens as the concentration of NH_4F increases. The reason is that low concentrations of F^- may

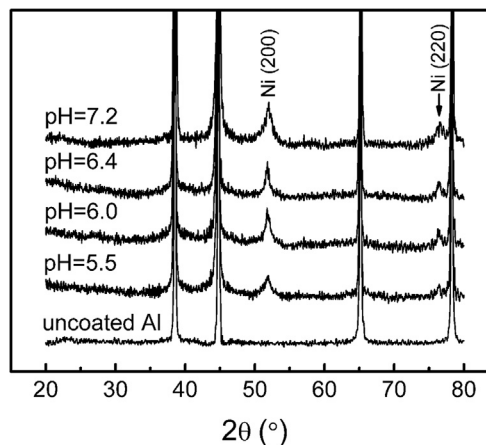Fig. 1. XRD patterns of raw Al and the Al/Ni products prepared at different pH values.