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Development of Spacecraft Black Thermal Control Coatings Using the Synthesized Mesoporous Co_3O_4 Pigment

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ABSTRACT

The thermo-optical properties of a coated surface are important for spacecraft thermal control coatings which depend on the optical properties and structure of the coating material. These coatings control the temperature by their capability of outer energy absorption and emission. The optical properties of pigment can be improved by generating a high fraction of voids in its structure. In this paper, mesoporous Co_3O_4 powders were successfully synthesized through hard template method using SBA-15. The resulting black pigment was characterized using BET, XRD and FE-SEM. The reflective property of Co_3O_4 was investigated by diffuse reflectance ultraviolet-visible near-infrared spectrophotometer. Reflectance measurement revealed that these mesoporous materials had high absorption characteristic (α_s=0.95). The resulting mesoporous Co_3O_4 was mixed with potassium silicate as transparent binder to coat Al substrate which shows high solar absorptance (α_s=0.94) and high thermal emittance (ε_t=0.96). The study indicated that Co_3O_4 coating may be a promising kind of black thermal control coatings. Prog. Color Colorants Coat. 8 (2015), 169-176 © Institute for Color Science and Technology.

1. Introduction

Protecting spacecraft and their working components from the harmful effects of extreme temperatures (a prime concern of design engineers) is no simple task. This is the main function of the spacecraft's thermal

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control system (TCS). The challenges imposed by the harshness of space become even more pronounced when one considers the extreme shifts in temperature endured as orbiting spacecraft repeatedly pass through day and night, a scenario referred to as "thermal cycling" [1]. To keep equipment temperature and optimize the devices performance, spacecraft surfaces are covered by thermal control coatings (TCCs) that have special thermo-optical properties (α_s and ε). The black thermal control coatings lead to surface warming while white thermal control coatings lead to surface cooling.

Several types of black pigments such as carbon black, magnetite, nonporous Co_3O_4 and metal nanoparticles have been reported for using in black TCCs [2]. Up to now, Co_3O_4 particles with different sizes and morphologies including tubes, rods, fibers, films, cubic and hexagonal single crystals in nanoscale have been prepared [3, 4]. Porous structure of metal oxide with a high surface area has been required for application in many fields [3]. Cobalt oxide is an important spinel-type structure which has a wide range of applications in various fields such as electrochromic devices, anode materials in Li ion rechargeable batteries, ceramics, pigments, heterogeneous catalysis, solid-state sensors, magnetism, solar energy absorbers and energy storage [5]. Porous cobalt oxide can be prepared via sol-gel [6], solvothermal [7] and hydrothermal [8] methods. The template methods are usually adopted for their preparation. The templates are classified as hard-core templates (such as the two dimensional (2D) hexagonal SBA-15 and three-dimensional (3D) cubic KIT-6) and soft-core templates (mainly supermolecular assemblies, such as emulsions, droplets, micelles and large molecule aggregates). However, cobalt oxide possesses some features like low cost and ease of mass production, stability at operating temperatures and good resistance to thermal shocks, oxidation, humidity, UV radiation and handling which make it one of the most promising metal oxides for use as a solar selective absorber [9].

In this work, new black thermal control coating based on mesoporous structured cobalt oxide (Co_3O_4) as pigment were prepared via employing silica source (SBA-15) as hard templates. Pigment particles were dispersed in silicate resin and then sprayed onto the aluminum (Al 6061) substrates. The purpose of this work was to investigate the new black thermal control coating with mesoporous Co_3O_4

2. Experimental

2.1. Materials

The potassium silicate solution was obtained from Merck. The characteristics of the resin are summarized in Table 1. Pluronic P123 triblock copolymer ($PEO_{20}PPO_{70}PEO_{20}$) as a structure-directing agent was purchased as commercially. Tetraethyl orthosilicate (TEOS), HCl, ethanol and $Co(NO_3)_26H_2O$ were purchased from Merck company.

2.2. Template preparation

Synthesis of SBA-15 Silica. SBA-15 silica was synthesized according to Zhao et al [10]. SBA-15 was prepared in HCl (2M) aqueous solution using tetraethoxysilane (TEOS) as the silicon source and Pluronic P123 triblock copolymer ($PEO_{20}PPO_{70}PEO_{20}$) as a structure-directing agent.

Table 1: characteristics of the pottasium silicate resin.

Sodium silicate solution	Concentration (%W/W)
SiO_2	60.26
K_2O	32.45
Solids content	31.74
SiO_2:K_2O weight ratio	1.857

In the synthesis of SBA-15 sample, 4.0 g of Pluronic P123 was dissolved in 120 g of distilled water and 120.0 g of HCl (2 M). Mixture was stirred for 1 h to complete dissolution; 8.50 g of TEOS was added at once. The mixture was left under stirring at 35 °C for 24 h, followed by a hydrothermal treatment at 100 °C for 48 h under static conditions. The solid product was filtered, washed with water or ethanol, and dried in air. Finally, the template was achieved by calcination under ambient condition from room temperature to 500 °C, with a heating rate of 1 °C/min, and a holding time of 6 h at 500 °C [10].

2.3. Preparation of mesoporousstructured cobalt oxide (Co_3O_4)

Typically, 1.0 g of SBA-15 was dispersed in 10 mL of 0.8 M solution of $Co(NO_3)_26H_2O$ in ethanol and stirred at room temperature for 1 h. Ethanol was removed by evaporation while heating at 80 °C. Afterward, the resulting powder of pink color was heated in an oven at 200 °C for 10 h to completely decompose the nitrate species. The impregnation and decomposition steps were repeated twice following the same conditions.

The resulting material was calcined at 450 °C for 6 h. The resulting sample was 4 times treated with a hot (2 M) NaOH solution to remove the silica template. The black Co_3O_4 material was recovered by centrifugation and finally dried at 50 °C followed by washing with water and ethanol several times, and then drying at 60 °C [7].

2.4. Paint preparation

A homogenous coating was prepared as follows: Co_3O_4 was incorporated into potassium silicate binder at pigment to binder mass ratio of 25:1 [11]. Pigment and binder were mixed together and the pigment particles were dispersed in binder with a pearl mill apparatus for 5 h. The prepared mixture was applied on aluminum sheet using a spray. After the coatings were fully dried, their reflectance and thermal emittance were measured.

2.5. Instruments

Diffuse reflectance spectroscopy (DRS) was measured using UV-Vis Spectrophotometer, JASCO, V-670 (190-2700 nm, Japan) in the range of 220-2200 nm to determine solar absorptance (α_s) according to ASTM E903 standard [12]. The thermal emittance of the films was measured by Temp 2000A infrared reflectometer (AZ Technology, USA) in the range of 3-30 μm according to ASTM E408 standard [13]. The morphology of coatings and pigments were examined using Hitachi S-4160 Field Emission Scanning Electron Microscopy (FE SEM) at an accelerating voltage of 15 kV. X-ray diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Co-Kα radiation (40 kV, 40 mA and λ=1.7890 Å).Nitrogen adsorption–desorption measurement was performed with a Micromeritics BELSORP-MAX instrument at 350 °C using Brunauer–Emmett–Teller (BET) calculations for surface area and Barrett–Joyner–Halenda (BJH) calculations for pore size distribution.

3. Results and discussion

3.1. FT-IR spectra

The fourier transform infrared (FT-IR) spectra of Co-SBA-15 and Co_3O_4 are shown in Figure 1. In the Figure 1a, the band at 1093 cm^{-1} corresponded to characteristic of anti-symmetric vibration non bridging oxygen atoms (Si-O) of Si-O-H bonds [14]. No IR band located at around 1090 cm^{-1} can be observed for the Co_3O_4 in Figure 1b. These FT-IR spectra show the complete elimination Si-O bonds after washing with alkaline solution.

3.2. X-ray diffraction

The low angle X-ray diffraction patterns of the precursor SBA-15 and mesoporous Co_3O_4 are compared in Figure 2. For SBA-15, three peaks with 2θ at 0.82°, 1.46°, and 1.7° indexed as (100), (110), and (200) reflections associated with *p6mm* hexagonal symmetry were observed, indicative of the well-ordered mesoporous structure of SBA-15 [15]. The low angle XRD patterns of Co_3O_4 also gave a strong (100) peak and weak (110) and (200) reflection peaks similar to the SBA-15 template. This indicates that Co_3O_4 is a perfect replica of SBA-15 [16].

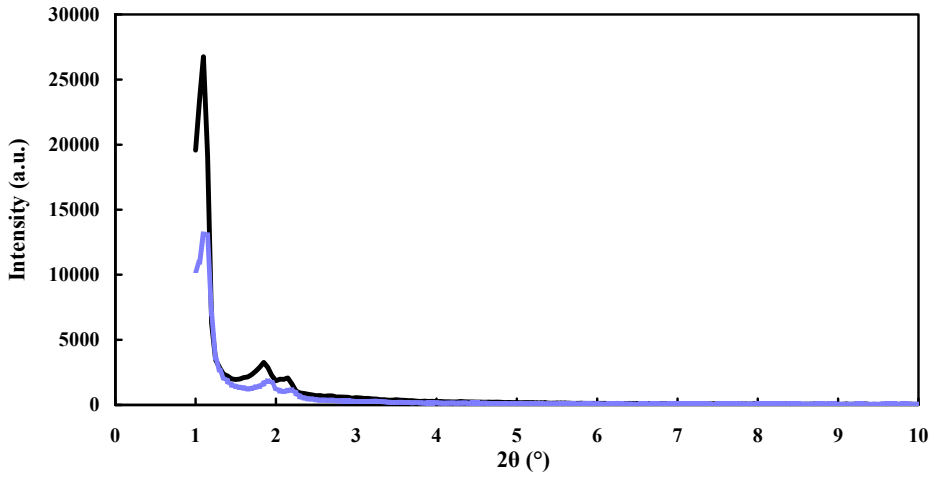

Figure 1: Low-angle XRD of mesoporous Co_3O_4 obtained at loadings Co-SBA-15 (a) Low-angle XRD of SBA-15(b).

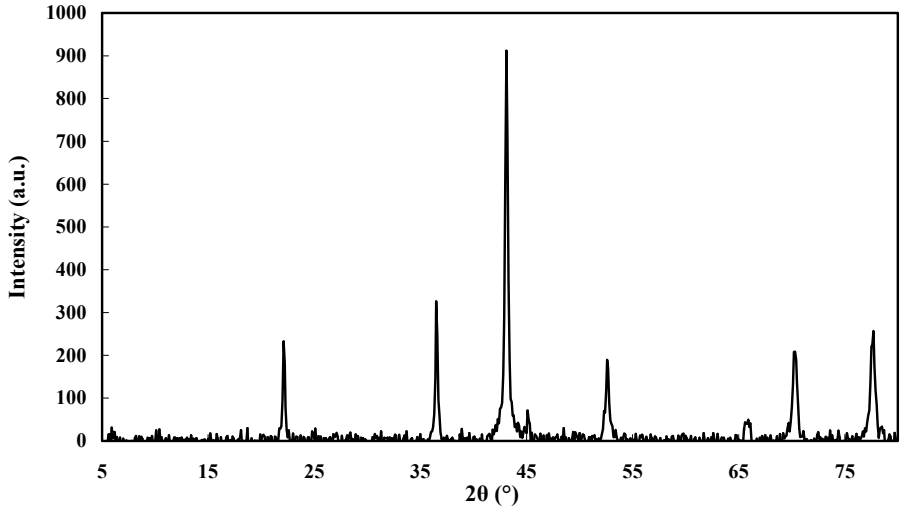

Figure 2: XRD pattern of Co_3O_4 powder.

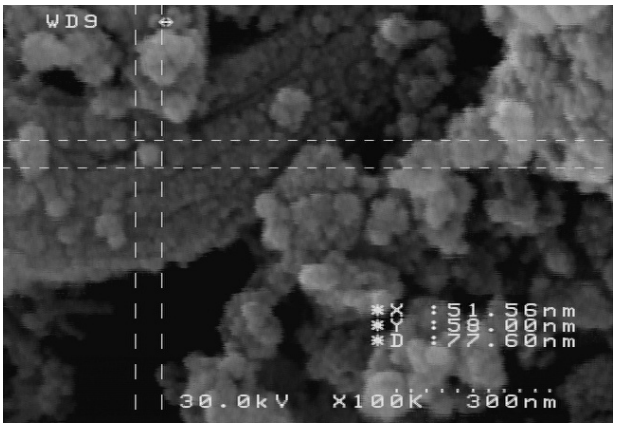

Figure 3: FE-SEM images of mesoporous Co_3O_4.

The XRD pattern of the Co_3O_4 powder is shown in Figure 3. All of the reflections shown in this Figure can be readily indexed to a 2D hexagonal structureof Co_3O_4. No characteristic peaks of impurity phases such as CoO and Co_2O_3 are present, indicating the high purity of the final products.The strong reflections at 2θ values of 21.9, 36.3, 42.9, 52.4, 70.1 and 77.5 degree were attributed to the typical diffraction peaks of spinel Co_3O_4 according to the definition of JCPDS card 42-1467.

3.3. Scanning electron microscopy

Figure 4 shows FE-SEM micrographs of the Co_3O_4 product as pigment after calcination. As seen in Figure 4, microsphere particles had very uniform morphology in a narrow particle size distribution, approximately 80 nm diameter.

3.4. Surface area and porosity

The porous product was confirmed by measurement of the surface area and pore size distribution, which was performed by the Brunauer–Emmett–Teller (BET) gas adsorption/desorption methods. Figure 5 shows adsorption/desorption isotherm and Figure 6 shows the pore size distribution of the mesoporous Co_3O_4. The type-IV isotherm with a typical H4 hysteresis loop in the range of 0.8-1.0 P/P_0 is obtained. Table 2 summarizes the textural data calculated from the isotherms. As seen in Table 2, the Co_3O_4 has porous structure, which is resulted from the interspaces of the constituent nanoparticles [17], which conforms to the FE-SEM observations. Quantitative calculation shows that the BET surface area of the mesoporous cobalt oxide is 68 m^2g^{-1}.

Figure 5 shows the pore size distribution of the mesoporous materials analyzed using the Barrett-Joyner-Halenda (BJH) algorithm method. Using the BJH algorithm from the desorption branch of the nitrogen physisorptionisotherms, 1 to 8nm pore radius range was obtained.

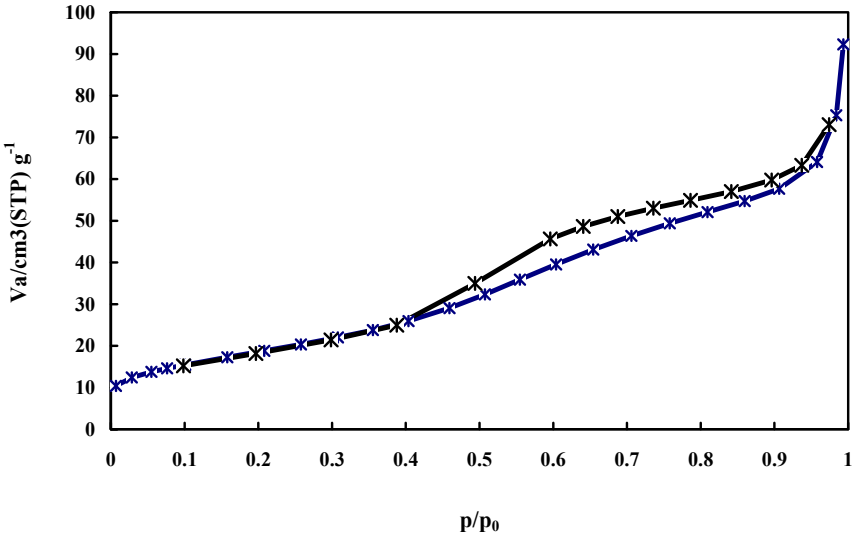

Figure 4: Nitrogen physisorption isotherms of mesoporous Co_3O_4.

Table 2: Nitrogen Physisorption Data from Mesoporous Co_3O_4.

Sample	template	S_{BET} (m^2 g^{-1})*	V_T (cm3 g^{-1})*	d_0 (nm)*
Co_3O_4	SBA-15	68	0.13	2

3. 5. Optical properties

Diffuse reflectance spectra (DRS) of as-synthesized porous cobalt spinel pigment and its prepared coating that was applied on the grounded aluminum substrate are shown in Figure 6. As indicated in Figure 6a, the reflectance of the pigment is below 3% at 220-800 nm. The reflectance has been increased with low slope in the NIR region, which provides 10% of the reflection. The reflection spectrum for applied coating is similar to the pigment (Figure 6b). Absorption coefficient (α_s) of the pigment and the prepared coating was calculated in accordance with ASTM E903-96 in the area between 220-2200 nm. The obtained results indicated that the coating with porous cobalt pigment has high absorption in this wavelength range, and porous cobalt spinel pigment and the coating containing this pigment have a high absorption coefficient α=0.95 and 0.94, respectively.

Coating prepared with potassium silicate binder and mesoporous cobalt spinel pigment, has a high thermal emittance (ε = 0.96), which is satisfactory for a black thermal control coating. In the present study, mesoporous cobalt oxide pigment in black thermal control coatings is used because of its higher absorption compared with other black coatings containing cobalt oxide pigments (Table 3) [18-21]. According to the results, broadband reduction in reflectivity over a larger range of incidence angles can be achieved using porous materials. Porous texturing of pigments can cause significant deviations in how light is reflected and scattered, leading to enhanced absorption over that of nonporous pigments. This improvement can be easily described using the principles of ray optics. Light can effectively become trapped in voids and holes where multiple reflections enhance the coupling into the material. Because of its porous structure, multiple internal reflections can guide the light into the bulk.

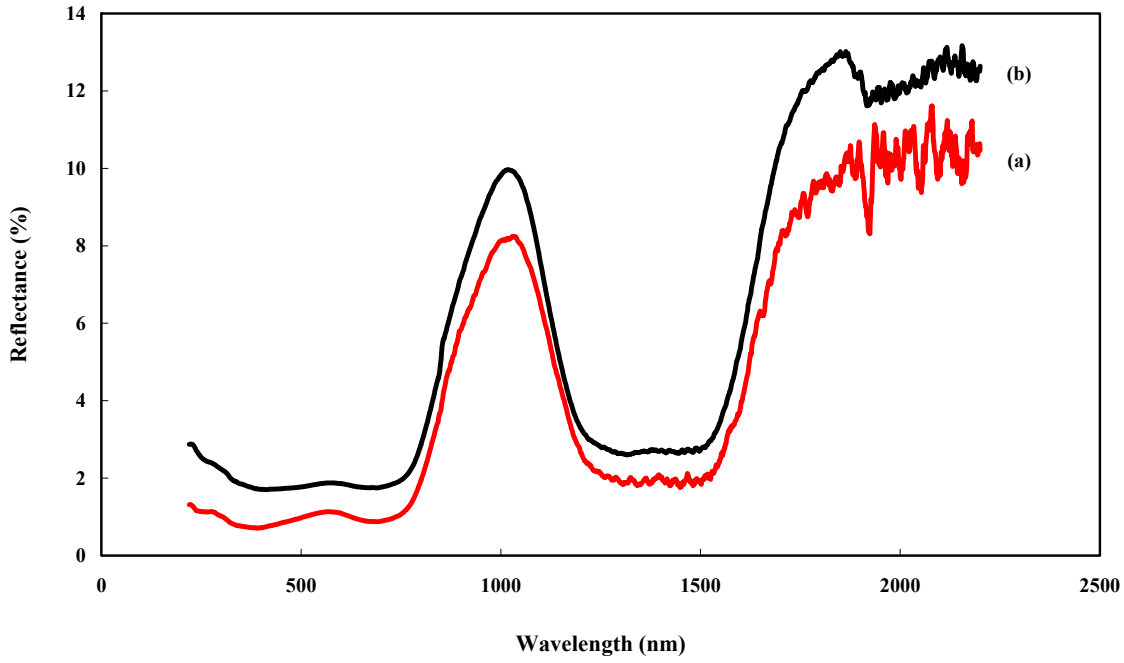

Figure 6: (a) diffuse reflectance spectra (DRS) of mesoporous cobalt oxide pigment and (b) DRS of Coating applied on to an aluminum substrate has been sanded.

Table 3: Comparison of the absorption coefficient of the coating containing Co_3O_4.

sample	α	reference
Co_3O_4/Al	0.92	[16]
Co_3O_4/SS*	0.9	[17]
Co_3O_4/SS	0.82	[18]
Co_3O_4/SS	0.93	[19]
Co_3O_4/Al	0.95	In this study

* Stainless Steel

4. Conclusions

In the present work, optical properties of mesoporous Co_3O_4 and its prepared coating using potassium silicate as binder have been studied and compared with common cobalt spinel. Coating can be prepared at low pigment to binder ratio (1:25) that led to reduction of final system weight. The results indicated that the prepared coating had a high absorption coefficient (α=0.94) and thermal emittance(ε = 0.96) with ratio of $\alpha/\varepsilon \approx 1$. Optical evaluation showed that this coating is suitable for using in black thermal control coatings.

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