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Al_2O_3-based pigments synthesized by a new proteic sol–gel method

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Abstract Alumina-based pigments were synthesized by the proteic sol–gel method. In this method, coconut water is employed as polymeric agent instead of the conventional alkoxide precursors. To this study, three common chromophore metallic ions (Mn^{3+}, Co^{3+}, and Cr^{3+}) were chosen in order to verify the method efficiency. Differential thermal analysis (DTA), thermogravimetry (TG), and XRD techniques were used to characterize the synthesis process. The colorimetric characterization of the produced pigments was done according to the CIE-L*a*b* 1976 norm which is recommended by the CIE (International Commission on Illumination). The synthesized pigments presented intense and uniform colors in accordance to the literature results for each chromophore ion. The produced pigments also presented agglomerated with an average grain size of 180 nm when calcined at 800 °C.

Keywords Proteic sol–gel · Coconut water · Alumina · Inorganic pigment

Introduction

Pigments can be defined as colored or white chemical compounds insoluble in the medium in which are dispersed. They can be subdivided in two main groups: inorganic and organic. In the inorganic group, we have the ceramic pigments which are composed by inorganic crystalline solids such as: hematite-, titanium-, alumina-, and zircon-based materials. It is well known that the pigment color is affected by several factors such as chemical composition, crystalline structure, point defects, grain size, homogeneity, and consequently by the synthesis method [1].

Alfa alumina-(α-Al_2O_3) based materials are very well-known pigments with important characteristics mainly in ceramic industry. Their main advantages are the high thermal and chemical stability, low cost and the possibility of obtaining a large range of colors according to chromophore ions. For example, manganese-doped alumina produces a pink color pigment [2] and chromium-doped alumina produces green or pink colors depending on the composition and thermal conditions [3, 4]. In particular, pigment based on a $Cr_{1.23}Al_{0.77}O_3$ composition is used in ceramic industry [4]. Several other colors which are Al_2O_3 based can be achieved using distinct chromophores ions with different concentrations [5–8].

Additionally, the proteic sol–gel technique is a promising method to obtain nanostructured powders in several ways [9, 10]. In this method, coconut water is employed as polymeric agent instead of the conventional alkoxide precursors. Therefore, in this study, we have studied the synthesis and characterization of the Al_2O_3-based pigments synthesized by the proteic sol–gel method. Three common chromophore metallic ions (Mn, Co, and Cr) were chosen in order to verify the efficiency of the synthesis method. Thermal analysis, structural, and colorimetric characterizations were also done.

Experimental procedure

The pigments were synthesized by the proteic sol–gel method [9, 10], using as precursor materials aluminum, manganese, cobalt, and chromium nitrates (P.A.). Figure 1

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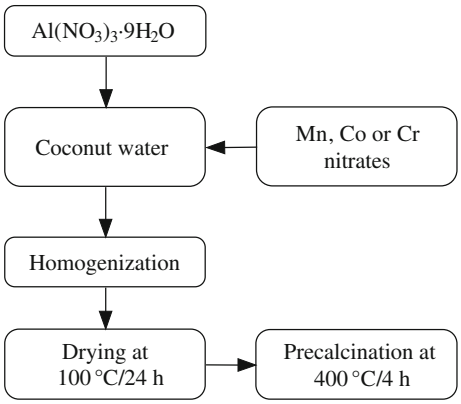

Fig. 1 Flowchart of the synthesis process by the Proteic sol–gel method

shows the flowchart of the synthesis process. In this method, the precursors are mixed with filtrate coconut water and homogenized by stirring until its complete dissolution (at room temperature). Following this dissolution, the solution was dried at 100 °C for 24 h, becoming a hygroscopic xerogel. Soon after, the xerogel was pre-calcined at 400 °C/4 h with a heating rate of 10 °C/min forming a black-spongy material. Finally, the powder was grounded in an agate mortar and calcined following a heating rate of 10 °C/min at different temperatures to obtain the crystalline and colored pigment. For this synthesis, a molar concentration of 2 M was used and three different pigments were prepared: Al_2O_3 with 1% of Mn^{3+} (AlMn), $Cr_{1.23}Al_{0.77}O_3$ (AlCr), and Al_2O_3 with 15% Co^{3+} (AlCo).

Thermal analysis of the dried resins at 100 °C/24 h was performed using a simultaneous DTA/TG (SDT 2960—TA Instruments) at a heating rate of 10 °C/min, in a flow of synthetic air (O_2/N_2—1/4), from the room temperature up to 1200 °C. The structural investigation and phase formation were done by powder X-ray diffraction technique in a XRD – Rigaku RINT 2000/PC, using Cu K_α radiation. The measurements were carried out at room temperature in the calcined powder, in continuous mode, in the 2θ range between 20° to 60°, and in steps of 0.02°. The morphological characteristics of the calcined powders were analyzed through Field Emission Scanning Electron Microscope (FEI Quanta 200 FEG).

The colorimetric characterization was done according to the CIE-L*a*b* 1976 norm which is recommended by the CIE (International Commission on Illumination). This norm describes all the colors visible to the human eye and the color can be represented by three coordinates: L* is the lightness of the color and can change from L* = 0 (black) to 100 (diffuse white); a* can change from negative to positive values corresponding to green and magenta colors, respectively; and b* can also change from negative to positive values corresponding to blue and yellow colors, respectively. The colorimetric measurements were carried out in reflectance mode using an UV–VIS-NIR Lightsource (DH-2000), an OceanOptics Spectrofotometer (HR 2000) and the SpectraSuite software, using the standard D65 illumination.

Results and discussions

Figure 2 presents the DTA/TG curves of the dried solutions of the AlMn (Fig. 2a), AlCo (Fig. 2b), and AlCr (Fig. 2c) samples. From these results, it was possible to subdivide the thermal decomposition in four stages. The first and second stages are characterized by two endothermic peaks and a high mass loss. These events can be attributed mainly to dehydration and denitration reactions. In the third stage, small exothermic peaks take place due to the organic decomposition reaction [10, 11]. It is important to note that these three stages occur in similar temperature range, indicating that these thermal events are faintly influenced by the dopante addition.

Figure 3 presents the XRD patterns as a function of the calcination temperature of the AlMn (Fig. 3a), AlCo (Fig. 3b), and AlCr (Fig. 3c) samples. In the AlMn sample, an amorphous phase was observed up to 700 °C, and only at 800 °C, the γ-Al_2O_3 phase was crystallized. Above this temperature, γ-Al_2O_3 to θ-Al_2O_3 and α-Al_2O_3 phase transitions were observed. A similar behavior was observed in the AlCo samples, but the γ-Al_2O_3 phase is crystallized at 500 °C and remains up to 1000 °C. After calcination at 1200 °C, it is also possible to see the crystallization of the θ-Al_2O_3, α-Al_2O_3, and $CoAl_2O_4$ phases. This increase in the temperature of the γ-Al_2O_3 to α-Al_2O_3 phase transition in Co-doped Al_2O_3 was related by Cava et al. [5]. According to the authors, cobalt has the possibility to be situated in tetrahedral and octahedral sites in γ-Al_2O_3, however, as α-Al_2O_3 is only constituted of octahedral sites, an additional energy is necessary to displace cobalt from tetrahedral sites, avoiding the γ-Al_2O_3 to α-Al_2O_3 transition and stabilizing $CoAl_2O_4$ spinel phase at lower temperatures. In both samples, a peak at about 35° (•) was also observed and is related to KCl phase from the coconut water. Besides, according to the literature, the presence of the θ-Al_2O_3 phase in these samples suggests a crystallite size smaller than 25 nm [12]. In the AlCr samples (Fig. 3c), the $Cr_{1.23}Al_{0.77}O_3$ phase was crystallized at 500 °C and remains stable for higher calcination temperatures [4]. This result is in accordance to the Cr_2O_3–Al_2O_3 phase diagram, which indicates that these two oxides can form a complete range of substitutional solid solutions below ~2100 °C.

Figure 4 presents a SEM image of the AlCr powder sample calcined at 800 °C/4 h. In this condition, the

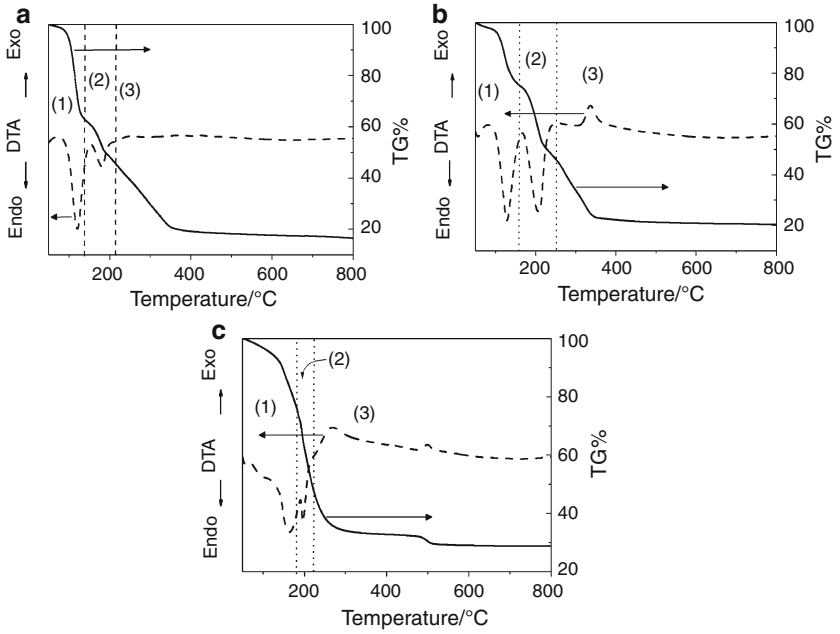

Fig. 2 DTA/TG curves of the dried solutions at 100 °C/24 h: **a** AlMn, **b** AlCo, and **c** AlCr

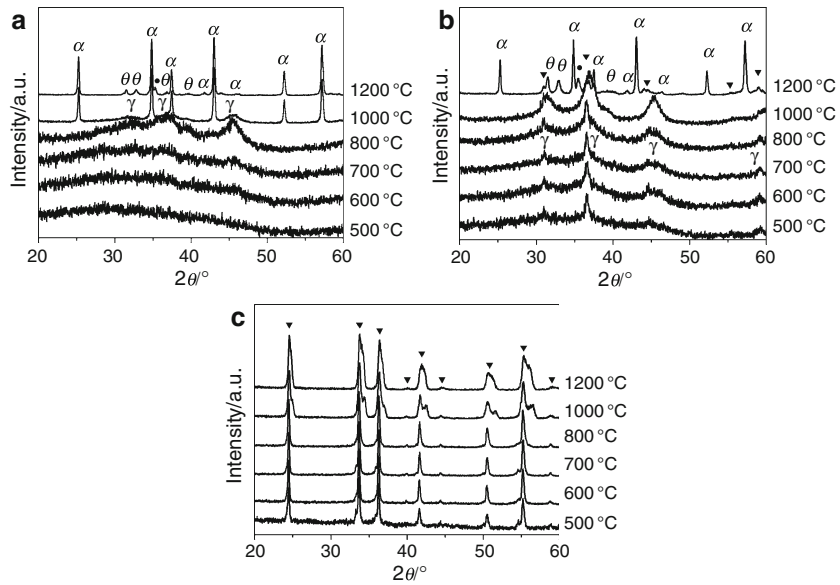

Fig. 3 XRD patterns as a function of the calcination temperature: **a** AlMn, **b** AlCo, and **c** AlCr. α: α-Al_2O_3 (PDF-431484); ***θ***: *θ*-Al_2O_3 (PDF-110517); *γ*: *γ*-Al_2O_3 (PDF-011307); *filled circle*: KCl (PDF-780656); *filled triangle*: $CoAl_2O_4$ (PDF-822252)

pigments presented very agglomerated and an average particle size of about 180 nm. Besides, neither significant difference was observed as a function of the composition range studied.

Based on this study, the powders were calcined at different temperatures and the produced pigments were characterized according to the CIE-L*a*b* 1976 norm, as described in "Experimental procedure" section. Table 1 presents the chromatic coordinates (L*, a*, and b*) of the synthesized pigments. To human eyes, manganese-doped Al_2O_3 pigments presented pink color; cobalt-doped Al_2O_3 pigments presented a shift of dark blue to blue color; and chromium-doped Al_2O_3 pigments presented a shift of dark green to green color. These colors already were expected according to the literature [2–5, 7]. Clearly the pigment colors change when the calcination temperature increases. This behavior can be attributed to the crystalline phase transition as observed by the X-ray results and by the increasing of the particle size. The synthesized pigments also presented intense and uniform colors and good stability after glazing at 1200 °C.

Besides these pigments presented here, several other compositions were also produced changing the Co, Mn, and Cr concentrations up to 25, 5, and 66 mol%, respectively. Others chromophore metallic ions were also used (not shown here), for example, Fe, Zn, Ni and mix of 2 or 3

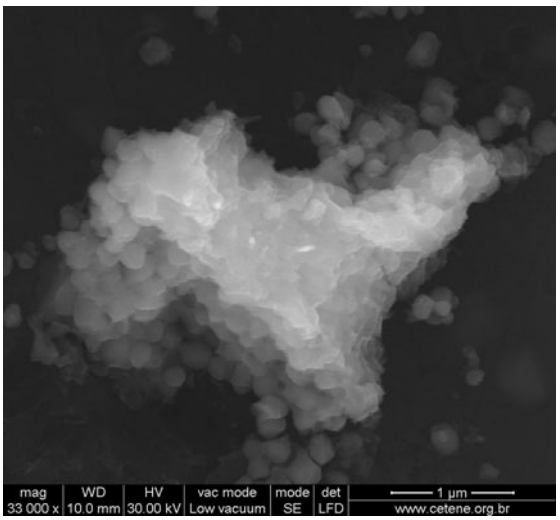

Fig. 4 SEM image of the AlCr sample calcined at 800 °C/4 h

Table 1 Chromatic coordinates (CC) of Al_2O_3-based pigments obtained by the Proteic sol–gel method

Composition	CC	Calcination temperature/°C					
		500	600	700	800	1000	1200
Al_2O_3:1%Mn (AlMn)	L*	67.6	66.2	74.5	74.1	78.6	89.6
	a*	6.2	6.8	8.1	7.5	12.5	13.0
	b*	12.5	13.1	14.9	15.4	21.1	17.1
Al_2O_3:15%Co (AlCo)	L*	57.1	54.3	54.1	48.9	51.0	63.7
	a*	−2.8	−3.0	−3.0	−4.7	−5.9	−4.8
	b*	2.5	5.3	−5.9	−13.0	−55.9	−50.1
$Cr_{1.23}Al_{0.77}O_3$ (AlCr)	L*	19.7	40.0	42.3	43.4	49.3	50.7
	a*	7.7	−7.6	−8.5	−5.3	−9.6	−7.9
	b*	23.2	20.0	20.2	22.7	16.2	10.2

doped ions in the same sample obtained different colors. These results will be presented and discussed in subsequent papers. Finally, according to ours results and observations, we have found that it is possible to produce many other colors using different chromophore ions with different concentrations by the proteic sol–gel method.

Conclusions

Alumina-based pigments were successfully synthesized for the first time by the proteic sol–gel method. It was observed a dependence on the thermal events and alpha–beta alumina phase transition with the chromophore ions employed. The synthesized pigments were characterized according to the CIE-LAB color space and presented intense and uniform colors in accordance to the literature results. Besides, according to our results and observations, we have found that it is possible to produce many other colors using different chromophore ions with different concentrations by the proteic sol–gel method.

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