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Influence of the pH on Al_2O_3:CuO Pigments Prepared by a Polymeric Precursor Method

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Copper (II) aluminate, $CuAl_2O_4$, which is known to be an inverse spinel contains a d^9 metal ion and possesses interesting electronic, magnetic and catalytic properties and is used in industry as ceramic pigments, coatings and catalysts. Al_2O_3 with 10 mol% Cu (AlCu10) was synthesized by the polymeric precursor method varying the pH of the precursor solution with addition of ammonium hydroxide and ethylenediamine. It was shown that the pyrolysis of the polymeric chain occurs in higher temperatures for samples prepared in higher values of pH. The colorimetric coordinates exhibit dependence with pH and with the increase of annealing temperature. AlCu10 samples prepared with higher values of pH present lower values of colorimetric coordinates, indicating alterations in its color. The luminosity parameters L* increase also as a function of pH.

Keywords: *Al_2O_3:CuO, pigments, polymeric precursor method*

1. Introduction

In the last years, the development of pigments for the production of tiles, ceramic coatings or cosmetics has become a need, because the aesthetic aspect and the color frequently represent the parameters of interest[1]. These parameters are modified through the changes in the coloring performance of pigments, that depends very much on their thermal stability, their chemical reactivity towards the glaze components, the coordination of host ions, and it also depends on the preparation methodology[2].

Many studies about nanoscale pigments has been achieved in the last years[3,4]. In the area of coatings and pigments, new approaches through nanoscale effects can be used to create coatings with significantly optimized properties. The conventional areas of its application are paints, building materials, plastics, enamel and ceramics[3]. For this purpose, many methods have been employed, among them the polymeric precursor method[3]. This method, also referred to as the Pechini method[5], allows the production of nanocrystalline powder samples at a relatively low temperature. This method consists of formation of a polymeric net starting from a polyhydroxy alcohol and an alpha-hydroxycarboxylic acid, with metallic cations homogeneously distributed throughout the matrix[6].

However, there are few works in the literature describing the influence of pH on synthesis of powders prepared by the polymeric precursor method[7-9]. To better understand this influence, the objective of the present work is to study the influence of pH on the synthesis of pigments.

It is known that copper(II) aluminate, $CuAl_2O_4$, which is known to be an inverse spinel contains a d^9 metal ion and possesses interesting electronic, magnetic and catalytic properties and is used in industry as ceramic pigments, coatings and catalysts[10]. Various methods have been employed to prepare $CuAl_2O_4$ material, such as fusion of the two component oxides at high temperatures, co-precipitation reactions in solution and sol–gel technique[10]. However, there are no studies about $CuAl_2O_4$ prepared via the polymeric precursor method as far as we know. Thus, Al_2O_3 with 10 mol% Cu was synthesized by the polymeric precursor method varying the pH of the precursor solution with addition of ammonium hydroxide and ethylene diamine. In this study, the samples were characterized by X-ray diffraction (XRD) technique, thermogravimetry (TG) and colorimetric measurement.

2. Experimental Procedure

The polymeric precursor method is based on the polymerization of metallic citrate by ethylene glycol. A hydrocarboxilic acid such as citric acid is normally used to chelate cations in an aqueous solution. The addition of a polyalcohol such as ethylene glycol leads to an organic ester. Polymerization promoted by heating to around 100 °C results in a homogenous resin in which the metal ions are distributed uniformly throughout the organic matrix.

Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and copper (II) nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) were used as precursors. The purity of these reagents was 98% (Synth). Aluminum nitrate and copper nitrate dissolved in water were added to an aqueous citric acid solution ($C_6H_8O_7.H_2O$ – Synth, 99.5%) under constant agitation. Ammonium hydroxide or ethylenediamine (Synth – PA) were added to the

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solution to adjust the pH to be around 1, 4 and 8. After this, ethylene glycol, $HOCH_2CH_2OH$ (Synth, 98%) was mixed in to promote the polymerization of the citrate by a polyesterification reaction. The citric acid:metal molar ratio was 3:1, while the citric acid:ethylene glycol ratio was 60:40 (mass ratio). The heat treatments to obtain the $CuAl_2O_4$ pigment powders were carried out in two stages: initial heating of the resin at 400 °C/h (10 °C/min) to pyrolise the organic material, followed by heating at 600, 800 and 1000 °C for 1 hour (10 °C/min) to eliminate residual organic material and formation of crystalline phases.

The thermal decomposition and crystallization process were studied by thermogravimetry (TG) (Netzch STA 409C) technique, after the first stage of the heat treatment, under oxygen atmosphere at a heating rate of 5 °C/min. Al_2O_3 compound was used as the reference material during the thermal analysis.

The powders were structurally characterized using an automatic diffractometer (Rigaku, Rotaflex RU200B) with Cu-Kα radiation (50 kV/100 mA, 1.5405 Å) and a graphite monochromator. The scanning range was between 10 and 70° (2θ) with a step size of 0.02° and a step time of 1.0 seconds. For this characterization, the powders were calcined at 600, 800 and 1000 °C during 1 hour to increase the degree of crystallinity.

Colorimetric coordinates and diffuse reflectance of the pigments were measured through the Konica Minolta spectrophotometer CM2600d, in the 350-750 nm range, equipped with standard light sources type A (tungsten lamp, 2800 K), C (halogen lamp, 6775 K), and D50 (day light), following the CIE-L*a*b* colorimetric method recommended by the CIE (Commission Internationale de l'Eclairage)[11]. In this method, L* is the lightness axis [black (0) - white (100)], b* is the blue (–) - yellow (+) axis, a* is the green (–) - red (+) axis, and ΔE is defined as the total color difference ($\Delta E^2 = L^{*2} + a^{*2} + b^{*2}$).

3. Results and Discussion

In this study, samples with composition 10 mol% Cu in the Al_2O_3 die (labeled as AlCu10) were used to study the influence of pH on the properties of the obtained material. Figure 1a presents the TG curves for samples synthesized in pH 1, 4 and 8 (labeled as P1, P4A and P8A respectively) with the addition of NH_4OH. For all samples, two thermal events are observed. The first, which start at around 100 °C, is attributed to elimination of H_2O and NH_3 formed during the complexation of metals and chain polymerization from isopropyl alcohol, acetic acid and NOx[12]. The second event starts at different temperatures for each sample: 390 °C for P1 sample, 435 °C for P4A sample and 460 °C for P8A sample. This thermal event is attributed to the burn of organic materials that were not eliminated during the first thermal treatment, as the -CO- and -COO- groups in polymeric degradation[12].

It should be noted that the organic elimination temperature increases with pH. This fact is because in basic medium the approach of citrate groups is bigger, promoting the polymerization when ethylene glycol is added in the material synthesis13.This bigger approach of citrates groups is related to the higher pitch of dissociating of citric acid molecules, whose dissociating reactions are improved for higher values of pH in water's solutions[14]. The same behavior was observed for samples synthesized with ethylenediamine, as can be seen in Figure 1b, which shows the TG curves for samples synthesized in pH 4 and 8 (labeled as P4E and P8E respectively). In these TG curves, the second event starts at 421 °C for P4E sample and 489 °C for P8E sample.

The XRD technique was performed to evaluate the structure in different annealing temperatures and values of pH in the synthesis, as can be seen in Figure 2. Figure 2a shows the X-ray diffraction patterns for sample P1 submitted to different annealing temperatures. The XRD data show that peaks related to crystalline phases are observed for samples annealed at 600 and 800 °C, although amorphous phases predominate for both samples. X-ray diffraction patterns for P1 sample annealed at 1000 °C exhibits a crystalline phase without amorphous phases. This indicates that a complete crystallization occurs at between 800 and 1000 °C.

Figure 2b shows the XRD results for the AlCu10 samples annealed at 1000 °C and prepared with different values of pH: 1 (P1), 4 and 8 with the addition of NH_4OH (P4A and P8A samples) and 4 and 8 with the addition of

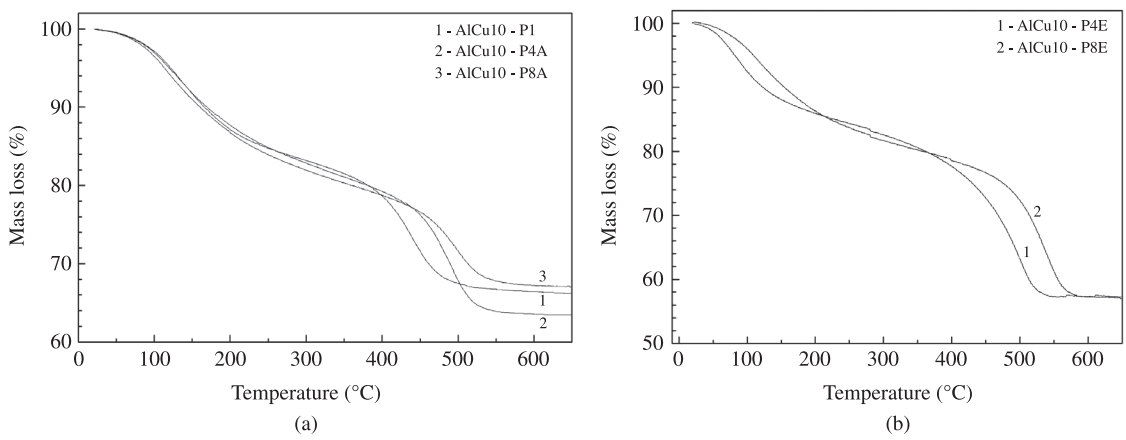

Figure 1. TG curves for the AlCu10 powder samples whose pH was adjusted with (a) NH_4OH and (b) ethilediamnina.

ethylenediamine (P4E and P8E samples). As can be observed in Figure 2b, these five samples exhibit identical X-ray diffractograms, indicating that there is no influence of pH in the crystalline structure of the AlCu10 samples at this annealing temperature.

Figure 2c presents the X-ray diffraction pattern for AlCu10-P1 sample annealed at 1000 °C. Al_2O_3[15] and $CuAl_2O_4$[16] phases were indexed and the peaks marked with asterisk are related to crystallographic plans of the $CuAl_2O_4$ phase. According to the literature, the Al_2O_3 presents a structure with a rhombohedral symmetry of R-3c space group and the $CuAl_2O_4$ presents a structure with a cubic symmetry of Fd3m space group. No other phase was identified and the amount proportion of Al_2O_3 and $CuAl_2O_4$ phases are 66% and 34% respectively.

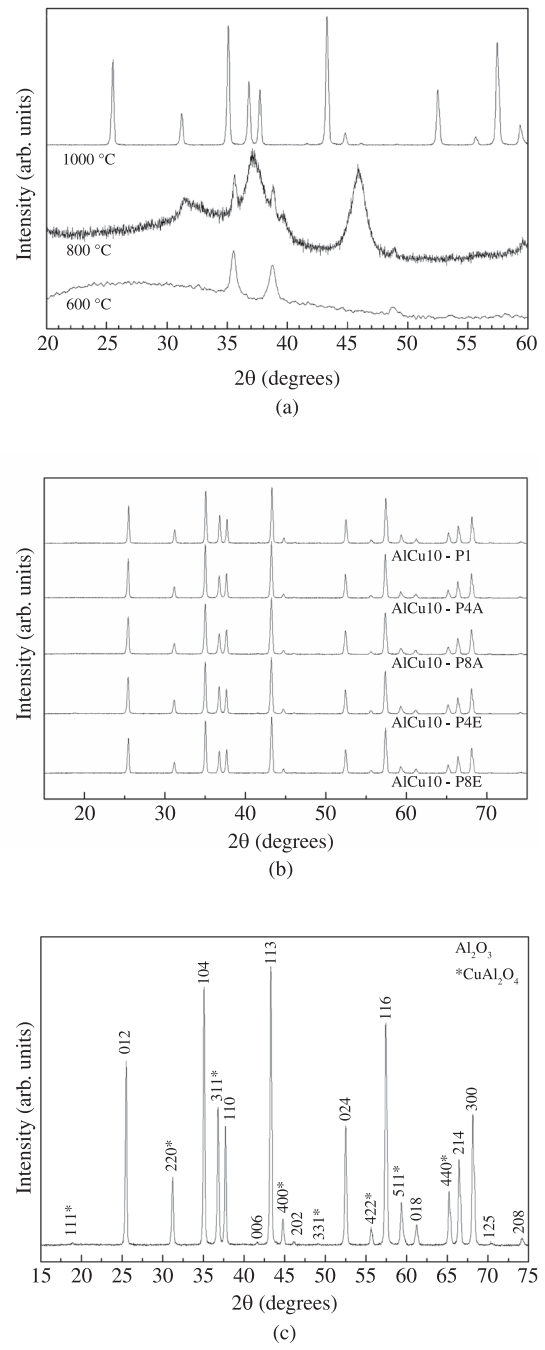

Figure 2. X-ray diffraction data for (a) AlCu10-P1 annealed at 600, 800 and 1000 °C, (b) AlCu10 samples annealed at 1000 °C at various pHs and (c) AlCu10-P1 with Al_2O_3 and $CuAl_2O_4$ phases identified. The peaks marked with an asterisk correspond to the $CuAl_2O_4$ phase.

Colorimetric analyses according to the CIE-L*a*b* standard colorimetric method were performed for AlCu10 samples synthesized at different pH annealing temperatures, whose results are presented in Table 1. As can be seen, AlCu10 samples annealed at 600 and 800 °C exhibit negative values of colorimetric coordinates a* and b*, which is located in the third quadrant indicating a mixture of green and blue colors. AlCu10 samples annealed at 1000 °C present positives values for the colorimetric coordinates (first quadrant), indicating a brown color. Also, colorimetric coordinates a* and b* are smaller for samples AlCu10-P4A, AlCu10-P8A, AlCu10-P4E and AlCu10-P8E in comparison with sample AlCu10-P1, indicating that the synthesis pH and the addition of NH_4OH or ethylenediamine influences the final color of the samples. The luminosity parameter L* shows values near to the black and the highest values were founded to samples with highest values of pH. It was also observed that L* decreases as a function of the annealing temperature. This dependence of L* with annealing temperature can be attributed to the higher crystallinity degree, as can be seen in XRD results.

The total color difference (ΔE) is a parameter used to compare two samples of the same color17.One important information obtained here is that each pigment powder showed very close values of ΔE even for the different excitation light sources (tungsten lamp in 2800 K, halogen lamp in 6775 K and day light). This result shows that each pigment presents the same visual color in differents types of illumination, a desirable characteristic in applications as ceramic pigments.

Figure 3 shows the diffuse reflectance spectra for AlCu10 samples which were calcined at 800 °C for 1 hour. It is possible to observe that the samples present a wide reflectance band around 500-520 nm, indicating

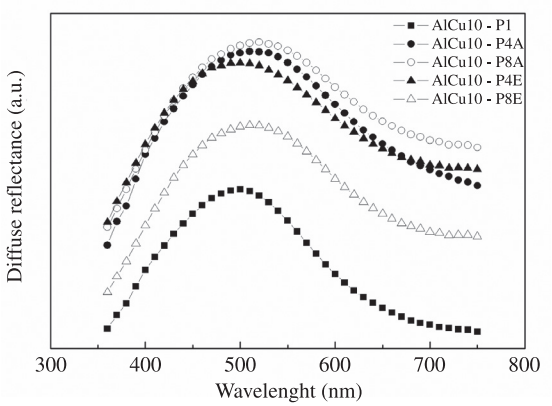

Figure 3. Diffuse reflectance spectra of the AlCu10 samples annealed at 800 °C.

a predominance of blue and green colors. According to the literature, the Cu^{2+} cation, with a $3d^9$ electronic configuration, exhibits one of the following structures: octahedral (blue color) or tetrahedral coordination (green color)[18]. Thus, it can be supposed that these two kinds of Cu^{2+} cation coordination are present at AlCu10 samples.

The reflectance band shows dependence with addition of ammonium hydroxide or ethylenediamine in the synthesis of AlCu10 samples. Samples prepared with ammonium hydroxide present the highest enlargement of reflectance band than samples prepared with ethylenediamine. The AlCu10-P1 exhibits the lowest enlargement.

Table 1. Colorimetric coordinates (L*, a*, and b*) and total color difference (ΔE) using light sources type A (tungsten lamp, 2800 K), C (halogen lamp, 6775 K), and D50 (day light) for the AlCu10 samples.

Sample	Light source	L*	a*	b*	ΔE
AlCu10-P1 600 °C	A	54.16	–3.18	–3.69	54.38
	C	54.63	–2.11	–3.01	54.75
	D50	54.53	–2.71	–3.13	54.68
AlCu10-P4A 600 °C	A	77.34	–13.51	–13.21	79.61
	C	79.32	–10.93	–9.38	80.61
	D50	78.91	–12.71	–10.30	80.58
AlCu10-P8A 600 °C	A	78.65	–11.43	–12.52	80.46
	C	80.40	–8.94	–9.26	81.42
	D50	80.03	–10.62	–10.03	81.35
AlCu10-P4E 600 °C	A	76.01	–13.30	–14.12	78.44
	C	78.02	–10.55	–10.29	79.40
	D50	77.60	–12.43	–11.21	79.38
AlCu10-P8E 600 °C	A	72.16	–16.70	–22.70	77.47
	C	74.98	–11.25	–17.85	77.89
	D50	74.35	–14.50	–18.99	78.09
AlCu10-P1 800°C	A	55.43	–0.18	5.70	41.05
	C	55.15	–1.07	5.60	41.27
	D50	55.24	–0.48	5.61	41.20
AlCu10-P4A 800 °C	A	77.93	–6.12	7.39	20.24
	C	78.17	–8.16	9.14	21.08
	D50	78.21	–7.27	8.64	20.66
AlCu10-P8A 800 °C	A	70.31	–5.33	4.83	30.05
	C	70.67	–4.82	7.15	30.09
	D50	70.64	–6.81	6.41	30.33
AlCu10-P4E 800 °C	A	65.21	–5.36	9.08	35.87
	C	65.60	–5.47	12.03	36.40
	D50	65.37	–7.64	10.70	36.58
AlCu10-P8E 800 °C	A	60.97	–10.34	2.10	39.91
	C	61.59	–8.21	5.31	39.14
	D50	61.93	–11.57	5.00	39.61
AlCu10-P1 1000 °C	A	53.42	13.41	18.94	51.64
	C	52.42	7.56	17.71	50.90
	D50	51.21	11.03	15.47	51.93
AlCu10-P4A 1000 °C	A	55.34	4.67	9.57	45.44
	C	54.96	1.73	9.74	45.64
	D50	54.47	2.58	8.66	45.95
AlCu10-P8A 1000 °C	A	59.76	11.49	18.11	45.21
	C	58.95	6.17	17.31	44.56
	D50	57.78	9.03	15.13	45.33
AlCu10-P4E 1000 °C	A	57.06	7.89	21.08	48.53
	C	56.01	14.24	19.92	49.54
	D50	54.67	11.65	17.40	49.53
AlCu10-P8E 1000 °C	A	47.84	14.34	22.76	58.29
	C	46.79	8.05	21.73	57.61
	D50	45.38	11.83	19.06	58.62

4. Conclusion

Ceramics pigments of Al_2O_3 with 10 mol% Cu prepared by a polymeric precursor method (Pechini) present different optical properties when synthesized at different pH values. It was shown that the pyrolysis of the polymeric chain occurs in higher temperatures for samples prepared in higher values of pH. However, alterations in the crystalline structure of the material are not observed as a function of the pH, or as a function of ethylenediamine or ammonium hydroxide addition.

The samples of this study heat treated at 600 and 800 °C present green and blue colors, whereas samples annealed at 1000 °C presents brown color. These differences are attributed to the fact that a complete crystallization occurs only in 1000 °C, whereas amorphous phases are still observed in samples annealed at 800 °C.

The colorimetric coordinates exhibit dependence with the value of pH and annealing temperature. AlCu10 samples prepared with higher values of pH present lower values of colorimetric coordinates, indicating alterations in its color. The luminosity parameters L* increase also as a function of pH.

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