Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 475–480

SYNTHESIS AND CHARACTERIZATION OF Al_2O_3/Cr_2O_3-BASED CERAMIC PIGMENTS

Maria I. B. Bernardi[1], *Samara C. L. Crispim*[2*], *A. P. Maciel*[1], *A. G. Souza*[2], *Marta M. Conceição*[2], *E. R. Leite*[1] *and E. Longo*[1]

[1]CMDMC, Departamento de Química, CCT, UFSCar, Rod. Washington Luis, Km 235,
São Carlos, SP, CP 676, 13565-905, Brazil
[2]LTM, Departamento de Química, CCEN, UFPB, Campus I, Cidade Universitária,
58059-900 João Pessoa, Paraíba, Brazil

Abstract

The synthesis and the characterization of Al_2O_3-based nanocrystalline inorganic pigments are reported. The pigments were synthesized by the polymeric precursor (Pechini method) using Cr_2O_3 as chromophore. XRD results only evidenced the corundum phase. The average particle size was about 34 nm. The samples were also characterized by differential scanning calorimetry (DSC) and thermogravimetry (TG), and CIE-L*a*b* calorimetry. The pigments obtained in this work presented different colors, ranging from green to rose.

Keywords: $Al_2O_3{\cdot}xCr_2O_3$, polymeric precursor, thermal analysis

Introduction

Corundum (α-Al_2O_3) is one of the most widely applied materials in ceramics. Such a huge use is due to its low cost and to its important mechanical, electronic and catalytical properties [1, 2]. In the recent years, there has been an increasing interest in the synthesis of nanocrystalline metal oxides. Nanocrystals are important for a variety of applications including fabrication of metal ceramic laminate composites and as a reinforcement phase in polymer and brittle matrix composites [3, 4]. Conventional methods for synthesizing α-Al_2O_3 powder involve solid-state thermally driven transformations from the hydrates of aluminum oxide. The extent of conversion to the corundum structure depends on the temperature and the time of thermal treatment, and total conversion occurs on heating above 1230°C [5].

Several factors and characteristics should be considered in the selection of pigments for a specific ceramic application. The most important of them are the thermal stability, the intensity and the uniformity of the obtained colors and the particle sizes of the powders.

---

* Author for correspondence: E-mail: samaracrispim@terra.com.br

1388–6150/2004/ $ 20.00
© 2004 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

After studying a $Co_xZn_{(7-x)}Sb_2O_{12}$ ceramic pigments [6] this work had as objective the synthesis by the polymeric precursor method of Al_2O_3-based inorganic pigments, doped with 1, 2 and 16 mol% of Cr_2O_3 and their characterization.

Experimental

The polymeric precursor solution was prepared by the Pechini method, which was used to synthesize polycationic powders. The process is based on metallic citrate polymerization using ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used to chelate the cations in an aqueous solution. The addition of a glycol such as ethylene glycol leads to the formation of an organic ester. Polymerizations, promoted by heating the mixture, results in a homogeneous resin in which the metal ions are uniformly distributed throughout the organic matrix. The metal sources used were $NH_4Al(SO_4)_2$ (Riedel) and $Cr(NO_3)_3\cdot 9H_2O$ (Aldrich), all with P.A. degree. The source of aluminum was dissolved in ammonium hydroxide – NH_4OH yielding aluminum hydroxide – $Al(OH)_3$, according to Eq. (1):

$$NH_4Al(SO_4)_2+3NH_4OH\rightarrow Al(OH)_3+(NH_4)_4(SO_4)_2 \qquad (1)$$

After the formation of the aluminum hydroxide precipitate, a paper filtering was made in order to completely eliminate the ammonium sulfate, the by-product of the reaction.

With the controlled addition of citric acid, the formation of aluminum citrate occurs. Next the metallic cation was added, which acts as chromophore, in the form of Cr_2O_3. The polymerization takes place upon the ethylene glycol addition. The citric acid/ethylene glycol mass ratio used was of 60/40. The pyrolysis of the resin is accomplished in oven, maintaining the temperature at 300°C for 1 h.

Three resins of Al_2O_3: 1, 2 and 16 mol% of Cr_2O_3 were synthesized, being submitted to thermal treatments (1000°C for 2 h) with different heating ratios (10 and 50° min^{-1}). A mixture of glaze and the sieved pigments (mass/volume ratio of the pigment: glaze equals to 12 g of pigments: 100 mL of liquid glaze) was homogenized in a ball mill during 10 min. The slip was poured on the ceramic biscuits obtaining a uniform glaze layer, which was then fired following a fast heat treatment (up to 500°C with heating ratio of 10°C min^{-1}, from 500 to 1180°C heated at 15°C min^{-1}, a plateau of 1180°C for 1 h and a cooling back to room temperature at 10°C min^{-1}).

The thermal effect of oxidation of the samples as well as the formation of the crystalline phases was studied by differential scanning calorimetric (DSC) and thermogravimetry (TG) (Netzsch, STA 440), under a synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of 10 and 50ºC min^{-1}. The reference material for DSC was Al_2O_3.

The determination the crystalline phases and the cell volume was carried out, using SiO_2 as an external standard, by X-ray diffraction (XRD) patterns. The equipment used was a Siemens D-5000 Diffractometer with CuK_α radiation (λ=1.5406 Å and θ=20 to 60°), operating at room temperature. By means of the pseudo-voigt functions, the X ray diffraction peaks profiles were used in order to estimate their exact full width at half maximum (FWHM) and the Scherrer equation was employed to the calculate crystallite sizes.

The L*, a* and b* color parameters of the enameled samples were measured through the Gretac Macbeth Color-eye spectrophotometer 2180/2180UV, using the D65 illumination. The CIE-L*a*b* colorimetric method, recommended by the CIE (Commission Internationale de l'Eclairage) [7] was followed. In this method, L* is the lightness axis [black (0)→white (100)], b* is the blue (–)→yellow (+) axis, and a* is the green (–)→red (+) axis.

Results and discussion

Thermal analyses (TG and DSC) were used with the same heating rate to observe the thermal behavior of these pigments, confirming thus an outstanding dependence of

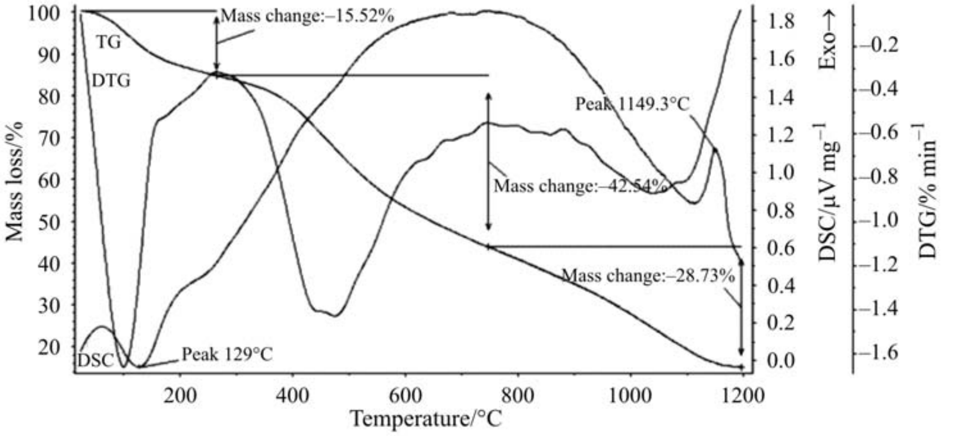

Fig. 1a TG/DTG and DSC curves for $Al_2O_3 \cdot 2\% \ Cr_2O_3$; 10°C min^{-1}, air

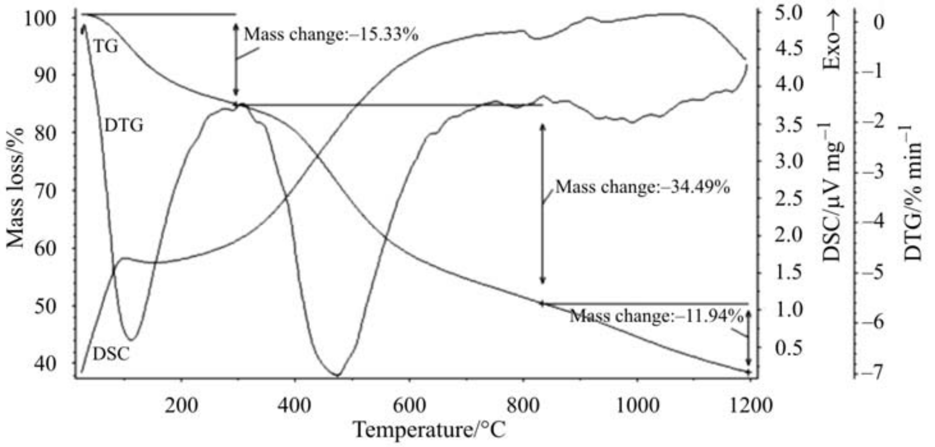

Fig. 1b TG/DTG and DSC curves for $Al_2O_3 \cdot 2\% \ Cr_2O_3$; 50°C min^{-1}, air

the color of the ceramic powders on such thermal behavior, as shown in Figs 1a and b (example of results the intermediate Al_2O_3·2 mol% of Cr_2O_3 resin).

The crystallization temperature of the α-Al_2O_3 diminishes upon the increase of the chromophore ion concentration, being observed for 1, 2 and 16 mol% at temperatures of 1165, 1150 and 1040°C. In the DSC curve an endothermic peak was observed at 572 and 582°C, which may be ascribed to the oxidation of Cr^{3+} to Cr^{4+} or may be related to the high concentration of chromium for this system, which may generate a metastable condition.

TG curves show three stages of mass losses: the first stage is attributed to the elimination of the adsorbed water. The second and third are attributed to the decomposition of the organic material. In Table 1 the results of the thermal analyses for all the studied samples are summarized.

Table 1 Results of thermal analysis for all of the samples

Sample/heating rate	TG		Phenomenon
	T_{range}/°C	Mass change/%	
Al_2O_3·1%Cr_2O_3 – 10°C min^{-1}	22–150	–11.19	In all cases: the first stage is attributed to the elimination of the adsorbed water. The 2nd and 3rd are attributed for decomposition of the material organic.
	150–801	–41.76	
	801–1156	–25.76	
Al_2O_3·1%Cr_2O_3 – 50°C min^{-1}	22–323	–13.42	
	323–964	–35.54	
	964–1196	–6.82	
Al_2O_3·2%Cr_2O_3 – 10°C min^{-1}	22–268	–15.52	
	268–772	–42.54	
	772–1196	–27.02	
Al_2O_3·2%Cr_2O_3 – 50°C min^{-1}	22–305	–15.33	
	305–838	–34.24	
	838–1196	–11.95	
Al_2O_3·16%Cr_2O_3 – 10°C min^{-1}	22–269	–10.69	
	269–796	–52.74	
	796–1190	–20.37	
Al_2O_3·16%Cr_2O_3 – 50°C min^{-1}	22–281	–10.83	
	281–682	–33.85	
	682–1195	–12.86	

Figure 2 shows the XRD patterns of $Al_2O_3 \cdot xCr_2O_3$ powder, in which (x=1, 2 and 16 mol%). It can be observed that the powders with 1 and 2 mol% at the Cr_2O_3, submitted to the heating rate of 10°C min^{-1} are amorphous. All the other samples were nanocrystalline (~34 nm) (T_c) with a high degree of crystallinity; presenting only the α-Al_2O_3 phase, Table 2.

Table 2 summarizes the results of the chromatic coordinates (L*, a* and b*) of $Al_2O_3 \cdot xCr_2O_3$ pigments obtained by the Pechini method presenting also the color and crystalline size of the powders.

Table 2 Chromatic coordinates of $Al_2O_3{\cdot}xCr_2O_3$ pigments obtained by the Pechini method, the color and crystalline size (T_c) the powders

Sample/heating rate	L*	a*	b*	Color	T_c/nm
$Al_2O_3{\cdot}1\%Cr_2O_3$ – 10°C min^{-1}	66.29	5.65	18.54	light green	amorphous
$Al_2O_3{\cdot}1\%Cr_2O_3$ – 50°C min^{-1}	67.48	10.63	6.28	rose	33
$Al_2O_3{\cdot}2\%Cr_2O_3$ – 10°C min^{-1}	65.24	4.37	16.60	light green	amorphous
$Al_2O_3{\cdot}2\%Cr_2O_3$ – 50°C min^{-1}	62.71	12.61	7.72	rose	33
$Al_2O_3{\cdot}16\%Cr_2O_3$ – 10°C min^{-1}	47.26	–2.90	14.75	dark green	35
$Al_2O_3{\cdot}16\%Cr_2O_3$ – 50°C min^{-1}	64.25	12.32	8.76	rose	34

It was observed that the powders treated with a heating rate of 10°C min^{-1} presented a green color with different intensities. The pigments obtained with 50°C min^{-1} presented a rosy color, intensifying it with the increase of the content of the chromophore ion. It should be noticed that both the increase of the chromophore ion content and the increase of heating rate during the thermal treatment increase the kinetics of the corundum phase nucleation and the lattice stresses, resulting in different colors.

The varieties of colors are produced by light absorption. This absorption is due mainly to electron transitions in long, conjugated systems. It is known that any color originates from electron transitions between the valence and the conduction bands. The band gap energy must also correspond to the characteristic wavelength of each color. It should be noted that the two features differ only in degree of energy level separation between filled and unfilled orbitals.

The mechanism involves electron excitation from the valence band to the conduction band. A transition-metal ion produces various colors depending primarily on the crystal field strength of a host matrix. One example is a Cr^{3+} doped into Al_2O_3. The increased in the chromium content causes the increase in the lattice constants of the

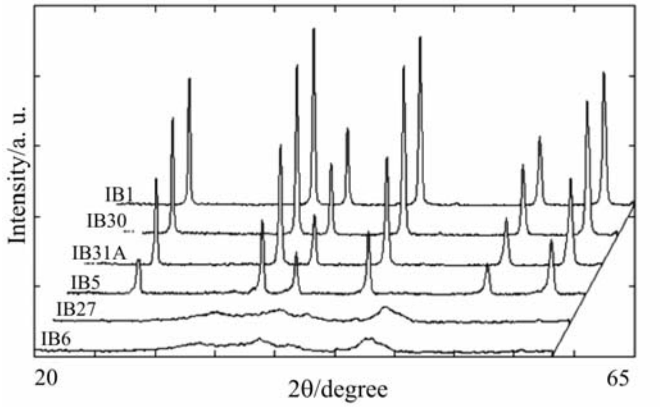

Fig. 2 XRD patterns of the $Al_2O_3{\cdot}xCr_2O_3$ powder, in which (x=1, 2 and 16 mol%) submitted to the heating rates of 10 and 50°C min^{-1}. For each pattern are indicated both the doping level and the heating rate

$Al_2O_3 \cdot xCr_2O_3$ solid solution, consequently, results in the decrease in the crystal field strength around the Cr^{3+} ion. The coloration of Cr^{3+} in Al_2O_3 changes with its content from purple, to purplish red, and finally to green. However, since a reddish color develops in the Al_2O_3–xCr_2O_3 system, Cr^{3+} cannot be excluded from red colorants. Cr^{4+}, however, is the focus of this effort to obtain red pigments [8–9].

The crystal field can be modified by adding an oxide that forms a solid solution with the host oxide due to the elongation or shrinkage of the host oxide lattice.

In the selection of the host oxide, symmetry of the host cation is a matter of important consideration, since the decrease in the degree of symmetry around the coloring ion enhances the transition probability between d orbitals, leading to a deepening of the coloration.

Conclusions

The Pechini method employed led to achieve a high degree of homogeneity at molecular level, as well as finer powders presenting thus higher surface areas. The color of the pigment is dependent of the state of oxidation of the chromophore ion. It was also shown that different concentrations of such chromophore ion and different heating rates play also an important role. As a consequence, rose and green pigments were obtained from the same Al_2O_3-based oxide system, doped with Cr_2O_3.

* * *

The authors acknowledge FAPESP, CAPES, CNPq and FINEP/PRONEX for the financial support.

References

1 R. K. Pati, J. C. Ray and P. Pramanik, Mat. Letters, 44 (2000) 299.
2 R. Uyeda, Prog. Mater. Sci., 35 (1991) 1.
3 A. Adak, A. Pathak and P. Pramanik, J. Mater. Sci. Lett., 17 (1998) 559.
4 P. Pramanik, Bull. Mater. Sci., 19 (1996) 957.
5 N. Ichinose, Superfine Particle Technology, Springer-Verlag, London, UK 1993.
6 D. S. Gouveia, A. G. Souza, M. A. M. A. de Maurera, C. E. F. da Costa, I. M. G. Santos, S. Prasad, J. B. de Lima, C. A. Paskocimas and E. Longo, J. Therm. Anal. Cal., 67 (2002) 459.
7 CIE, Recommendations of Uniform Color Spaces, Color Difference Equations, Phychometrics Color Terms. Supplement no. 2 of CIE Publ. No. 15 (E1-1.31) 1971, Bureau Central de la CIE, Paris 1978.
8 K. Nassau, The Physics and Chemistry of Color, Wiley, New York 1983, pp. 77–106.
9 F. Ren, S. Ishida, N. Takeuchi and K. Fujiyoshi, Ceram. Bull., 71 (5) (1992) 759.