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SYNTHESIS OF ZrO_2-BASED CERAMIC PIGMENTS

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Abstract

The pigments used in ceramic applications are of nature predominantly inorganic and they should be thermally stable, insoluble in glazing, resistant to the chemical and physical agents' attacks. This work aimed at the synthesis by the polymeric precursor method of ZrO_2-based inorganic pigments, doped with Fe, Ni, Co, Cr and Cu cations. The fired pigments were characterized by thermogravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction (XRD). Among the metals used to zirconium-doping, the best result was achieved with the cations Cu, which presented the monophase pigment, even as 20 mol% of dopant. Up to the temperature of 1000ºC the pigments presented a good thermal stability.

Keywords: pigments, thermal analysis, ZrO_2

Introduction

Among the possible coloration methods, the most effective way to supply and to establish a stable coloration to a ceramic product is the use of a pigment. The pigments are of great importance in the development of new lines of ceramic for coverings.

The pigments are organic or inorganic substances, used thoroughly in the coatings of surfaces, in paints of writing, in plastics, among other applications, to attribute coloration to the materials. The pigments used in ceramic applications are of nature predominantly inorganic and they should be thermally stable, insoluble in glazing, resistant to the chemical and physical agents' attacks, they should present an appropriate particle size and they should not produce emanations of gases in glazing that contains them and ought to display the uniformity of the obtained colors [1–7]. The research on modern pigments, now it is addressed to the development of pigments with larger reproducibility. For so much, chemical syntheses are being used (Sol–gel, Pechini) that result in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix, with pigment characteristics [1, 3, 4, 7]. This

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work had as objective the synthesis by the polymeric precursor method of ZrO_2-based inorganic pigments, doped with Fe, Ni, Co, Cr and Cu cations and their thermal and structural characterization.

Experimental

The polymeric precursor solution was prepared by Pechini process [1], which is used to synthesize polycation oxides powders [2, 3]. This process, outlined in Fig. 1, is based on metallic citrate polymerization with the use of ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used to chelate cations in aqueous solution. The addition of a glycol, such as ethylene glycol, leads to organic ester formation. Polymerization, promoted by heating the mixture, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix. The reagents used were PA degree.

Figure 2 summarizes the preparation of the ZrO_2 polymeric precursor mixture. A water solution of zirconium citrate was prepared separately [8]. The amount of citric acid is determined by the molar ratio citric acid/metal cations and was fixed, in this work, to 3:1. These citric solutions were then mixed (at $T \cong 70°C$) and ethylene glycol was added only at the end of the process, after the dissolution of cations (chromophore ions). The citric acid/ethylene glycol mass ratio was fixed to 60:40. The final mixture was dried for 40 min (at $T \cong 110°C$) to obtain the resin. The powders were calcined at 1000ºC in ambient air and kept at the annealing temperature for 1 h. The heating and cooling rates used were 10°C min^{-1}.

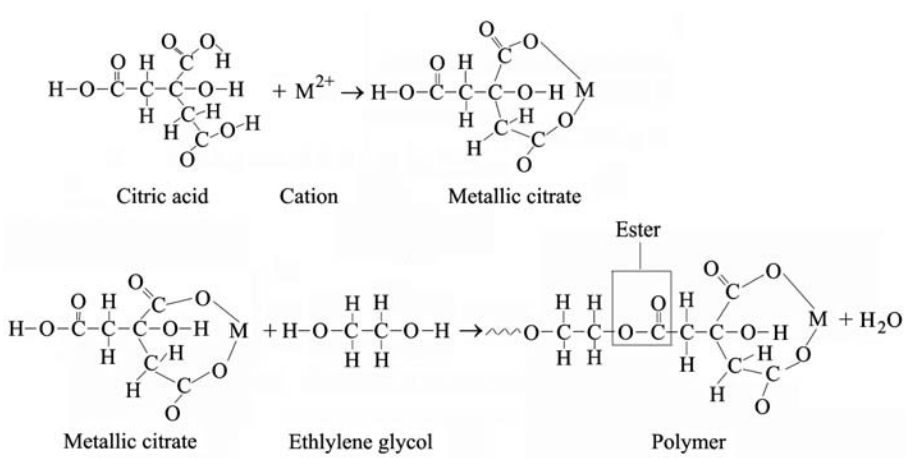

Fig. 1 Schematic representation of the Pechini method

The determination of crystalline phases was performed 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 75°), operating at room temperature. The thermal effect of oxidation of the samples, as well as the formation of crystalline phases was studied by

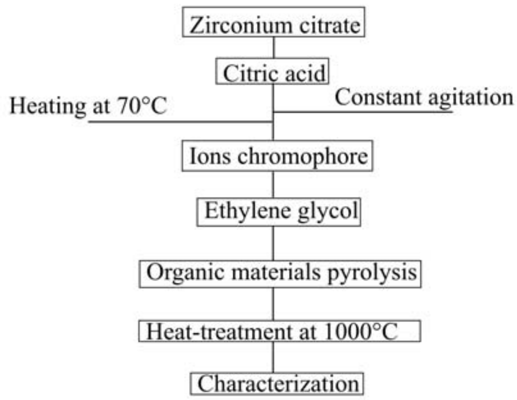

Fig. 2 Flowchart of preparation of the ceramic pigments using the polymeric precursor method

thermogravimetry (TG) (Shimadzu, TGA-50) with heating rate 10ºC min^{-1}, atmosphere of air with flow of 20 mL min^{-1} and mass of the sample of 7 mg, up to 900°C. The curves of differential thermal analysis (DTA) (Shimadzu, DTA-50) were obtained with heating rate of 10ºC min^{-1}, air static atmosphere and mass of the sample of 8 mg, up to 1150°C. The reference material for DTA was Al_2O_3.

Results and discussion

Figures 3–5 show the XRD patterns for the samples of ZrO_2-doped with the different metallic cations. The baddeleyite (ZrO_2) is observed as main phase, independently of the metals-doping and of their concentrations. Ni and Co presented two different phases: baddeleyite and their respective oxide (NiO and Co_3O_4). The samples doped with Fe presented segregation of different phases of iron oxides (Hematite and Maghemite: α-Fe_2O_3 and γ-Fe_2O_3). Among the metals used to zirconium-doping, the

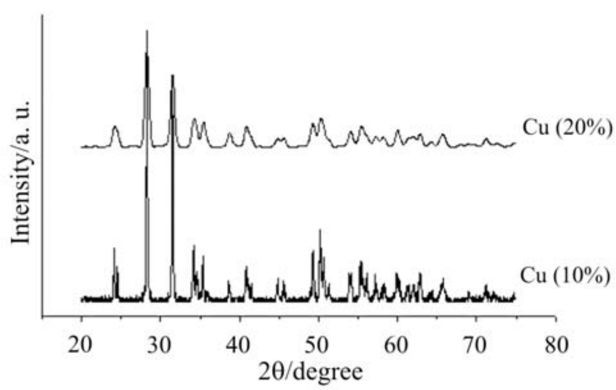

Fig. 3 XRD patterns of powder for ZrO_2:10 and 20 mol% Cu

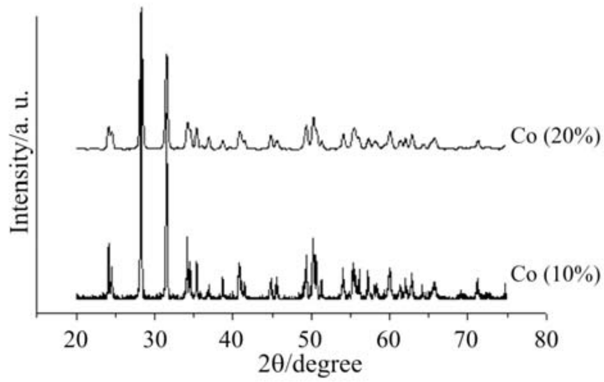

Fig. 4 XRD patterns of powder for ZrO_2:10 and 20 mol% Co

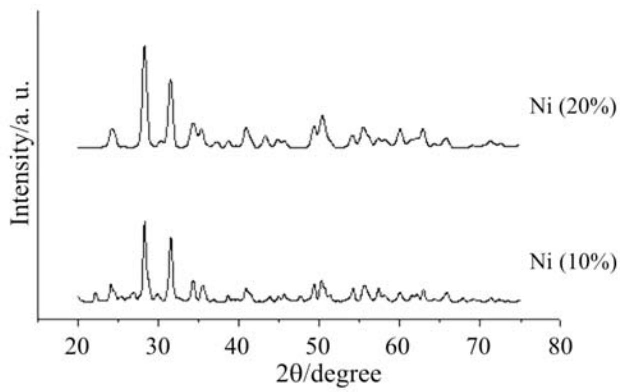

Fig. 5 XRD patterns of powder for ZrO_2:10 and 20 mol% Ni

cations Cu gave the best result, which presented the monophase pigment, even as 20 mol% of dopant, as shown in Fig. 3.

The TG curves of all samples showed three events of mass loss: the first event (28–300°C) was attributed to the elimination of the adsorbed water. The second (300–500°C) and third (above 500°C) events were attributed to the breakage of the organic chains and total thermal degradation.

On the TG/DTA curves (Fig. 6) it was observed that all samples showed exothermal reactions during the oxidative thermal decomposition, due to several events of thermal decomposition of the organic material.

The profile of the TG curves of all samples is similar irrespectively of the cation-doping and the percentage of the cation doped (Fig. 7).

The ceramic pigments obtained presented the following colorations according to Table 1.

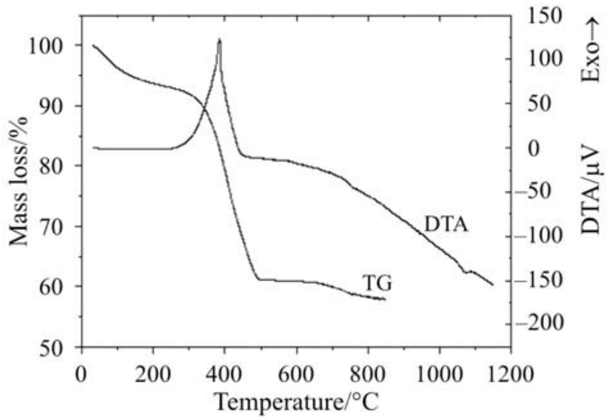

Fig. 6 TG/DTA curves of the powder (puff) ZrO_2:10 mol% Cu

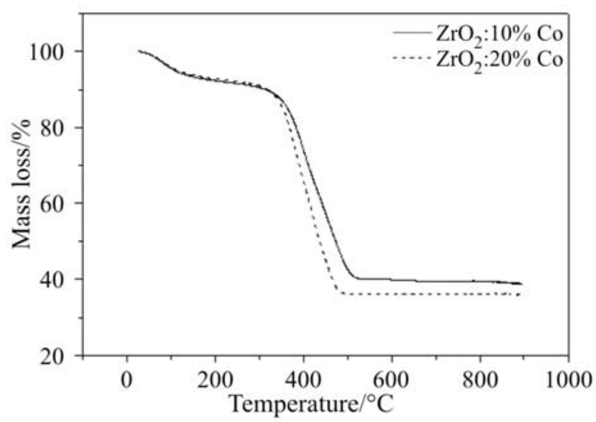

Fig. 7 TG curves of the powder (puff) ZrO_2:10 and 20 mol% Co

Table 1 Pigments color in agreement with the chromophores ions

Systems	Coloration
ZrO_2:20 mol% Cu	gray
ZrO_2:20 mol% Co	black
ZrO_2:20 mol% Ni	yellow
ZrO_2:20 mol% Cr	green
ZrO_2:20 mol% Fe	red

Conclusions

The synthesis and the characterization of ZrO_2-based inorganic pigments are reported. The pigments were synthesized by the polymeric precursor (Pechini Method) using Cu, Ni, Co, Fe and Cr as chromophores.

Baddeleyite (ZrO_2) is observed as main phase, independently of the metals-doping and of their concentrations. Ni and Co presented two different phases: baddeleyite and their respective oxide (NiO and Co_3O_4). The samples doped with Fe presented segregation of different phases of iron oxides (hematite and maghemite: α-Fe_2O_3 and γ-Fe_2O_3). Among the metals used to zirconium-doping, the best result was achieved with the cations Cu, which presented the monophase pigment, even as 20 mol% of dopant.

The profile of the TG curves is similar not reflecting the cation-doping and the percentage of the cation doped. Up to the temperature of 1000ºC the pigments presented a good thermal stability and an intense color characteristic of each metal doped.

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