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Micronizing ceramic pigments for inkjet printing: Part II. Effect on phase composition and color

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Abstract

Drop on demand ink-jet printing is turning to be the leading technique in the decoration of ceramic tiles. This technology makes use in most cases of pigmented inks which are manufactured by micronizing conventional ceramic pigments in the 0.2–0.6 μm range (median diameter). Although significant improvements to optical properties are in theory put forth by reducing the pigment particle size, not all the expected advantages occur and still unanswered questions concern the color strength of micronized pigments. This is the second part of a study aimed at disclosing what happens during pigment micronizing; it is focused on phase composition and color in the submicrometric field. For this purpose, representative industrial pigments were selected: Cr–Sb-doped rutile (orange–yellow), Co–Cr–Fe–Mn–Ni spinel (black), and V-doped zircon (turquoise–blue). Such pigments were micronized in a pilot plant and characterized for particle size and morphology (SEM and HR-TEM), phase composition, crystallite size and unit cell parameters (XRD-Rietveld), optical properties (DRS) and color after application in glazes for porcelain stoneware tiles fast fired at 1200 °C (CIE $L^*a^*b^*$). Results highlight a different behavior during micronization: crystal structural and optical features are substantially changed once pigment particles turn into submicronic size. A gradually lower particle dimension is accompanied by reduction of crystallite size and increasing frequency of lattice defects (inferred from variation of unit cell parameters and optical properties) up to amorphization that may attain 75 wt%. The formation of amorphous phase takes place below a critical crystallite size (30–40 nm) which discriminates two regimes with fast and slow comminution rates. These structural changes are associated to decreasing color strength and increasing brightness through the submicrometric field.

Keywords: A. Milling; B. Grain size; B. Microstructure-prefiring; C. Color; Amorphization

1. Introduction

Drop on Demand Ink-Jet Printing (DOD-IJP) is becoming the most popular technology for decorating ceramic tiles, gradually replacing conventional methods such as screen printing or silicon roller printing [1,2]. The driving force behind this technological innovation is discussed in the first part of the present study [3], which reports both the numbers of inkjet printers now in operation around the world and the advantages of DOD-IJP. In this second part of the study, we looked at what happens when ceramic pigments are micronized in terms of their phase composition and optical and technological properties. Micronization is the preferred method for obtaining the submicronic particle sizes needed for use in inkjet print heads [4,5]. This is currently done by means of high-energy ball milling at plants designed to reduce pigments' particle size and simultaneously ensure a thorough mixing of the colorant, carrier and additives, which are the basic ingredients of ceramic inks [5,6]. This one-pot process is used to obtain a finished ink that must satisfy the physical and chemical requirements of inkjet printers to ensure an adequate image quality (viscosity, surface tension, density, and color strength) and avoid issues such as nozzle clogging or sedimentation (particle size, drying behavior, and stability in storage) [7–9].

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There is an abundance of literature on high-energy ball milling, but it essentially focuses on mechanochemical synthesis/alloying, i.e. "a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill" that is "capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases" [10]. The micronizing process used for ceramic inks should, in principle, avoid any pigment reaction: in a way, it represents the early stage of mechanochemical alloying. Despite the growing interest in the mechanosynthesis of oxides – including those investigated in the present study, i.e. zircon, spinel and rutile [11–14] – little attention has been paid to this early stage in the relevant literature.

Micronized pigments (of submicrometric particle size) offer technological advantages over conventional micrometric pigments because of their larger surface area, which assures a higher surface coverage, a larger number of reflectance points and a consequently better scattering [15]. Used to decorate ceramics by ink-jet printing, they can overcome problems caused by nozzle clogging or dispersion instability. The coloring performance of ceramic pigments (which is their most important feature) depends on their optical properties and their chemical stability during the firing stage. The former are believed to improve in submicronic particles, while the rate at which they dissolve in glazes is expected to increase per specific surface area of pigment [16]. In theory, the optical properties of micronized pigments should change in that light absorption increases moving from micrometric to submicrometric sizes, while light scattering peaks at about half the light wavelength, i.e. 200–400 nm, which is more or less the target size for pigmented inks [15]. The expected benefits are not always apparent in industrial practice; however, and there are still questions to answer concerning the color strength of micronized pigments [6,7].

The aim of the present work was to see what happens to pigments when they are micronized and the effects on subsequent steps in the tile-making process. Three representative ceramic pigments used in DOD-IJP (spinel, zircon and rutile) were characterized in depth after simulating their industrial processing (high-energy ball milling, application on glaze, and firing) in the laboratory.

2. Experimental

Industrial pigments were selected to represent crystal structures with different physical properties relevant for their comminution behavior: vanadium-doped zircon $ZrSiO_4$:V (TZ) was selected, instead of the largely utilized praseodymium-doped yellow zircon, because the optical bands of V^{4+}, responsible of its turquoise color [17,18], allow to investigate better possible damages to color centers in the crystal structure. In the case of spinel (BS), a popular black pigment with composition in the Co–Cr–Fe–Mn–Ni system [19,20] was considered. For rutile (OR), the choice went on a typical orange–yellow pigment [21,22] doped with chromium and antimony (TiO_2:Cr,Sb).

The micronization process was simulated in a pilot plant (Netzsch Labstar LS1) keeping carrier, solid load, type and concentration of dispersant, temperature, rotation speed, amount and size of grinding media and milling time under control (details are reported in the first part of this study [3]). Specimens of pigment suspension were collected at increasing milling times and dried in oven (105 ± 5 °C) for mineralogical, optical and colorimetric analyses. Pigments were characterized by the following techniques.

Particles morphology and microstructure were characterized by scanning electron microscopy (SEM, Zeiss SUPRA 50 VP) and transmission electron microscopy (TEM, JEOL JEM 2100F).

X-ray powder diffraction measurements were carried out using a Bruker D8 Advance diffractometer equipped with a LynxEye detector (Cu Kα 1, 2 radiation) in the 10–80° 2θ measuring range, with an equivalent counting time of 16 s per 0.02° 2θ step. Quantitative phase analysis was performed using GSAS-EXPGUI software by RIR (Reference Intensity Ratio, using corundum as internal standard at 20 wt%) and Rietveld refinement techniques. Up to 50 independent variables were refined: phase fractions, zero point, 15 coefficients of the shifted Chebyschev function to fit the background, unit cell parameters, profile coefficients (one Gaussian, Gw, and one Lorentzian term, Lx). The experimental error is within 5% relative. Crystallite size was determined by Scherrer's equation, using the EVA software (Bruker) and subtracting the instrumental broadening assessed by measuring the LaB_6 reference material.

Optical measurements were performed by diffuse reflectance (Perkin-Elmer λ35 spectrophotometer, 400–1100 nm range, 0.1 nm step size, $BaSO_4$ integrating sphere, white reference material: $BaSO_4$ pellet). Reflectance (R_∞) was converted to absorbance (K/S) by the Kubelka–Munk equation: $K/S=(1-R_\infty)^2\times(2R_\infty)^{-1}$. Absorbance bands were deconvoluted by gaussian function (PFM, OriginLab) to obtain the band energy (centroid) and intensity (peak area) which experimental error, including background correction and reproducibility, is within 1%.

Color was measured by a Hunterlab Miniscan MSXP4000 spectrophotometer (CIE $L^*a^*b^*$ coordinates, where $C^*=(a^{*2}+b^{*2})^{0.5}$) after application (5 wt% pigment) in glazes for porcelain stoneware tiles fast fired at 1200 °C.

3. Results and discussion

3.1. Phase composition of pigments

The as-received TZ sample contained some unreacted precursors along with the zircon pigment, i.e. baddeleyite (monoclinic ZrO_2) and quartz (α-SiO_2), as is usually the case in industrial products [23]. This baseline composition remained substantially the same during the early stages of micronization, until a critical point in the milling curves was approached, as explained in the first part of the present study [3]. This was a point where the slope of the particle size versus milling rounds curve changed abruptly. Beyond this point, which occurred at about 60,000 rounds for zircon inks, there was an evidence of zircon (and quartz) amorphization (Fig. 1A). The proportion of the amorphous phase rapidly reached ~20 wt%, then rose slowly up to 25 wt% with longer milling times. The amorphization rate was similar for zircon and quartz, while the baddeleyite seemed to be less affected by prolonged milling. An alternative interpretation is that zircon might be broken down into ZrO_2 (baddeleyite) and SiO_2 (amorphous), as sometimes reported [11,24]. Zircon amorphization has been well documented in the