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Formulation and characterization of black ceramic ink for a digital ink-jet printing

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ABSTRACT

Formulation of black ceramic ink and its ink-jet printability on a glass substrate were investigated. The thermal and chemical stabilities of $CoFe_{2-x}Cr_xO_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ black inorganic pigments were analyzed with various amounts of Cr substitutions. The ceramic ink was prepared using the pigment composition that demonstrated color stability during the high temperature glazing process with a minimal Cr substitutional amount. After the dispersion stability and rheological property were optimized, the ceramic ink was suitably jetted from a print head as a single sphere-shaped droplet without satellite droplets. To improve the printability of the ceramic ink, the glass substrate was treated with a perfluorooctyl trichlorosilane (PFTS) solution. As a result, the PFTS surface treatment increased the contact angle of the ceramic ink droplets on the glass substrate and effectively minimized the ink spreading phenomena.

1. Introduction

Ink-jet printing technology, which is based on digitally controlled ink droplets from a print head, is attractive due to its capability of direct and fine printing onto various substrates [1,2]. Recent development of ink materials has expanded the application of ink-jet printing for various industrial manufacturing purposes [3]. In the ceramic industry, the need for the ink-jet printing technique using ceramic ink has also increased for the decoration of porcelain, glass, and ceramic tile products [4].

Compared with conventional ceramic decoration processes, ceramic ink-jet printing has many advantages in manufacturing ceramic products [5,6]. The ink-jet printing process is a fully digital process that enables printing of customized patterns and images with high resolution and efficiency. There is no direct contact point between the printer nozzle and substrate, thus printing can be processed on various kinds of objects that are difficult with the conventional decoration methods. In addition, the highly efficient use of ceramic ink can minimize the waste of raw materials, making ink-jet printing an eco-friendly process [7–9].

Ceramic ink-jet printing requires cyan, magenta, yellow, and black ceramic inks, which are the primary colors of digital printing. These ceramic inks are generally composed of inorganic pigments as colorants and an ink solvent for jetting. The inorganic pigments need to be highly dispersible in the ink solvent to prevent nozzle clogging and thermally stable above 1000 °C during the firing process in ceramic product manufacturing. The ink solvent needs to have appropriate viscosity and surface tension for a suitable jetting from the print head [10–12].

Here, we report the formulation black ceramic ink for a digital ink-jet printing process. Black inorganic pigments of various compositions were synthesized, and their color stabilities were characterized with a glazing process at high temperature. The ceramic ink was formulated with optimization of the pigment dispersion stability and rheological behavior. The jetting property and ink-jet printability of the formulated ceramic ink on a glass substrate was also investigated in detail.

2. Experimental

2.1. Preparation of inorganic pigments

Black inorganic pigments of $CoFe_{2-x}Cr_xO_4$ (x = 0, 0.1, 0.3, 0.5) and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ (x = 0, 0.1, 0.3, 0.5) compositions were synthesized using a solid state reaction. Cobalt oxide (CoO, Sigma aldrich), iron oxide (Fe_2O_3, Junsei), chromium oxide (Cr_2O_3, Junsei), nickel oxide (NiO, Sigma aldrich), and manganese oxide (MnO, Mn_2O_3, Sigma aldrich) were used as starting materials for the pigment synthesis. The starting materials were mixed using ball milling for 3 h and then calcined at temperatures from 800° to 1400°C for 1 h. High temperature color stability of the obtained pigments was investigated after

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the samples were mixed with transparent glaze and fired at 1250 °C for 1 h. The composition of transparent glaze includes 56.1 wt% of feldspar ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), 19.6 wt% of limestone ($CaCO_3$), 13.5 wt% of silicastone (SiO_2) and 10.8 wt% of kaoline ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$).

The crystal structure of the synthesized pigments was characterized using X-ray diffractometer (XRD, Rigaku, D/2500VL/PC). The morphology and diameter of the pigment particles were analyzed using a field emission scanning electron microscope (FE-SEM, Jeol, JSM-6390). To investigate the color properties of the pigments after calcination and glazing, CIE $L^*a^*b^*$ colourimetric parameters were measured by a spectrophotometer (CM-700D, Konica).

2.2. Formulation of ceramic ink

The prepared inorganic pigment was micronized using attrition milling to prevent nozzle clogging for the ink-jet printing application. Then, the pigment particles were dispersed in a mixed solvent of ethanol and ethylene glycol with addition of cetyltrimethylammonium bromide (CTAB) as a dispersant.

The viscosity and surface tension of the formulated ceramic ink were measured by a rheometer (Hakke mars III, Thermo scientific) and tension meter (DST60, Surface electro optics), respectively. The dispersion stability was evaluated using turbiscan (Turbiscan LAB, Formulaction). Turbiscan backscattering was analyzed by measuring the backscattered near infrared beam (880 nm) from the ceramic ink as a function of sample height. The ceramic ink was scanned with 0.04 mm scan step from 0 mm (bottom) to 40 mm (top). The measurement was carried out with 4 h time intervals for 24 h at 45 °C.

2.3. Ink-jet printing of ceramic ink

A soda-lime glass slide (60 × 25 × 3.8 mm) was used as a substrate for ink-jet printing. Prior to the printing process, the glass substrate was cleaned using ultrasonication and dried at 80 °C. Then, the glass substrate was immersed in a toluene solution with 5 vol% concentration of perfluorooctyl trichlorosilane (PFTS, Sigma aldrich) to lower the surface energy of the glass substrate and prevent ink spreading phenomena.

The jetting behavior and printability of the ceramic ink were analyzed using a dropwatcher (Cera DW, STI). The contact angle between the substrate and ceramic ink droplet was measured by a contact angle analyzer (PHX300, Surface electro optics). The ceramic ink was printed on the glass substrate using a print head (QS-256/80 AAA, Fujifilm dimatix) with a nozzle diameter of 35 μm. The ink-jet printed pattern on the glass substrate was observed by an optical microscope (SZ61, Olympus).

3. Results and discussion

Black inorganic pigments of $CoFe_{2-x}Cr_xO_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ compositions were synthesized at various calcination temperatures and Cr substitutional amounts. To characterize the temperature dependent crystal structures of the black inorganic pigments, XRD patterns of $CoFe_{1.5}Cr_{0.5}O_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.375}Cr_{0.5}Mn_{0.125}O_4$ pigments calcined at a temperature range from 800° to 1400 °C were carried out. The crystal structure of $CoFe_{1.5}Cr_{0.5}O_4$ pigment in Fig. 1(a) shows that Fe_2O_3 hematite phase of the starting material still remained after calcination at 800 °C, and a single spinel phase of $CoFe_{1.5}Cr_{0.5}O_4$ was observed from the pigments calcined above 1000 °C. Similarly, XRD spectra of $Ni_{0.925}Mn_{0.075}Fe_{1.375}Cr_{0.5}Mn_{0.125}O_4$ in Fig. 1(b) indicate that NiO and Fe_2O_3 hematite phases of the starting materials were present in the pigment calcined at 800 °C due to an incomplete solid state reaction. A spinel phase of $Ni_{0.925}Mn_{0.075}Fe_{1.375}Cr_{0.5}Mn_{0.125}O_4$ started to be formed at 1000 °C, and the single spinel phase was obtained above 1200 °C.

Cr substitutional amount in the pigment composition was controlled to improve the color and crystal structure stabilities of the black pigments during calcination and glazing at high temperature. Fig. 2 shows XRD spectra of $CoFe_{2-x}Cr_xO_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$. XRD analysis results in Fig. 1 confirm that the calcination temperatures of $CoFe_{2-x}Cr_xO_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ pigments were optimized at 1000 °C and 1200 °C, respectively. Regardless of Cr substitutional amount in the pigment compositions, all the as-prepared inorganic pigments were black colored powder which showed a single spinel phase without a secondary phase from the unreacted starting materials. In addition, the pigment particles were partially agglomerated during the high temperature calcination process, and the effect of Cr substitution on the overall pigment morphology was not clearly observed.

Figs. 3 and 4 show the color stability of the prepared black inorganic pigments after calcination and glazing, respectively. Generally, colored inorganic pigments are used at a high temperature with glazing for surface protection and an additional decoration effect of ceramic products. Thus, the inorganic pigments should be thermally and chemically stable. In Fig. 3, all the synthesized inorganic pigments with various Cr additions are generally black after high temperature calcination. However, the black color of the glazed inorganic pigments was not stably maintained according to Cr substitutional amount. The optically black color was only observed when Cr substitutional amount was higher than 0.1 in $CoFe_{2-x}Cr_xO_4$ and 0.5 in $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ compositions after glazing. $CoFe_2O_4$ pigment had a dark blue color and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ pigments with a low Cr amount was brown as shown in Fig. 6.

The effect of the glazing process on the pigment color was quantitatively analyzed through CIE $L^*a^*b^*$ measurement. The results of colorimetric analysis of as-prepared and glazed samples of $CoFe_{2-x}Cr_xO_4$ and $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ with various Cr amounts are displayed in Fig. 5. The intensity of the black color is mainly governed by the L^* value, which is the parameter corresponding to brightness. A low L^* value indicates that the pigment color is close to black, while a high L^* value indicates a bright color. The positive and negative a^* value means green and red, respectively. The positive and negative b^* values indicate a color ranging from yellow to blue. Generally, the values of a^* and b^* of the black pigment are negligibly small.

The L^* value of as-prepared $CoFe_{2-x}Cr_xO_4$ pigment decreased with an increasing Cr substitutional amount, resulting the pigment color close to black. The glazed $CoFe_2O_4$ pigment showed a slightly blue color due to the negative b^* value. After Cr substitution, a^* and b^* values decreased to close to zero, and the L^* value also decreased from 28.8 to 23.6. However, the color of $Ni_{0.925}Mn_{0.075}Fe_{1.875-x}Cr_xMn_{0.125}O_4$ pigments with a low Cr amount were unstable during the glazing process as shown in Fig. 4(b). The L^* and b^* values of the glazed pigment without Cr substitution significantly increased from 10.6 and 0.2–54.4 and 21.3, which is close to a yellow color. Cr substitution lowered L^* and b^* values, and black color started to be observed from the glazed pigment of $Ni_{0.925}Mn_{0.075}Fe_{1.375}Cr_{0.5}Mn_{0.125}O_4$ composition.

Then, $CoFe_{1.9}Cr_{0.1}O_4$ composition, which showed the stable black color in the glaze with a minimized Cr amount, was selected for the formulation of ceramic ink for ink-jet printing. The obtained black inorganic pigment was micronized into particles of below 300 nm in diameter using attrition milling to prevent nozzle clogging of the ink-jet print head. Fig. 6(a) and (b) present the overall morphologies of the black inorganic pigments during the attrition milling process. The as-synthesized pigment particles were generally irregular polygon shaped and partially agglomerated due to the high temperature calcination process. The pigment particle size initially showed a broad distribution from approximately 100 nm to 10 μm. PSA results in Fig. 6(c) and (d) indicate that the average particle diameter was significantly decreased in the initial 2 h of the milling process. Most of the pigment particles were smaller than 300 nm in diameter after 3 h of milling. The effect of the milling process on the pigment color was also quantitatively analyzed using CIE $L^*a^*b^*$ measurement. The measured $L^*a^*b^*$ values of