PREPARATION AND CHARACTERIZATION OF SPINEL MCr$_2$O$_4$ (M = Zn, Co, Cu and Ni) BY COMBUSTION REACTION

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Abstract. The ceramic industry applies many natural and synthetic pigments as coloring agents in glasses, enamels and unglazed bodies. The purpose of the present work was to prepare a series of chromium spinels MCr$_2$O$_4$ (M = Zn, Co, Cu and Ni) by combustion reaction, using urea as fuel and characterizing the resulting powders. The compositions were prepared by a single step solution combustion reaction using nitrates and urea as fuel. The fired pigments and enameled samples were characterized by X-ray diffraction, BET, scanning electron microscopy (SEM), UV-VIS-NIR spectroscopy, and CIE-$L^*a^*b^*$ color-measurements. The results demonstrated that synthesis by the combustion reaction was very fast and safe, resulting in crystalline spinel with nanoparticles in all the compositions under study. The pigments obtained by combustion reaction displayed better solubility in the molten glazes than pigments obtained by mechanical mixture of oxide precursors. The results demonstrate the viability of using the powders obtained as ceramic pigments.

Introduction

Pigments are defined as particulate solids, which may be organic or inorganic, white, black, colored or fluorescent, that are insoluble in the substrate in which they become incorporated and that do not react chemically or physically with this substrate [1, 2]. Pigments should present well defined optical and physical properties. These properties, in turn, depend directly on the pigment’s crystalline structure, on its physical (particle shape, distribution, and degree of agglomeration) and chemical characteristics (purity and stability of the composition). The most important characteristic to be considered in a pigment is its capacity to develop color (its pigmentary capacity) [3]. The control of these properties is closely dependent on obtaining nanometric scale particle sizes, i.e., obtaining molecular structures at the atomic level. The most common form of obtaining pigments is the conventional one of mixing oxides, although several other chemical methods allow one to obtain nanometric material with highly controlled purity and chemical homogeneity. Some of the most well-known methods are sol-gel [4], micro-emulsion [5], co-precipitation [6], supersonic radiation [7], Pechini’s method [8], hydrothermal synthesis [9], freeze-drying [10], and combustion synthesis [11-13].

Among the aforementioned methods of chemical synthesis, combustion reaction synthesis stands out as an alternative and promising method for obtaining after-ceramics on a nanometric scale. This synthesization method, also known as auto-propagating synthesis, allows for particles to be obtained (without pre-sintering) in sizes in the order of 30nm [14]. Compared to other synthesis methods, the combustion reaction process offers the advantages of being simple, fast, without requiring subsequent intermediary calcination stages, and consuming less energy during the synthesis [11]. Moreover, using the non-conventional method of combustion reaction results in the synthesis of highly pure, chemically homogeneous powders, which usually generate products with the desired structures and composition due to the high homogeneity aided by the solubility of the salts in water, allowing...
nanometric-sized particles to be obtained. Pigments are industrially processed by the conventional ceramic oxide mixing method, which, though economic, does not allow for the easy control of homogeneity and purity, mainly because it involves mixing and grinding processes. In this context, the purpose of this work was to apply combustion reaction synthesis to produce and characterize “spinel”-type inorganic pigments, specifically $MCr_2O_4$-type ($M$ is a divalent metal of the type $Ni^{2+}$, $Zn^{2+}$, $Cu^{2+}$ and $Co^{2+}$) ceramic oxides.

**Experimental**

Combustion reaction synthesis involves a mixture of metallic ions (nitrates) as oxidizing reagents and a fuel as the reducing agent. For this redox mixture, nickel nitrate - $Ni(NO_3)_2$, $6H_2O$, copper nitrate - $Cu(NO_3)_2$, $6H_2O$, zinc nitrate - $Zn(NO_3)_2$, $6H_2O$, cobalt nitrate - $Co(NO_3)_2$, $6H_2O$, chromium nitrate - $Cr(NO_3)_3$, $9H_2O$ and urea - $CO(NH_2)2$ were used. The proportion of each reagent was defined according to its respective molar amounts. Four compositions were studied, as follows: $Zn01$ ($ZnCr_2O_4$); $Ni01$ ($NiCr_2O_4$); $Cu01$ ($CuCr_2O_4$); $Co01$ ($CoCr_2O_4$). Stoichiometric compositions of metal nitrate and urea were calculated based on the components’ total oxidizing and reducing valences, which serve as the numerical coefficients for the stoichiometric balance, so that the equivalence ratio $\Phi_e$ is unity and the energy released is maximum [15]. Carbon, hydrogen, chromium, nickel, copper, zinc and cobalt were considered reducing elements with respective valences of $+4$, $+1$, $+3$, $+2$, $+2$, $+2$ and $+2$. The oxygen was considered an oxidizing agent with a valence of -2. The valence considered for nitrogen was 0.

The prepared solutions were mixed in a Pirex-type becker and heated directly on a hot plate at 480$^\circ$C until self-ignition occurred. The resulting powdered pigments, which had porous flake structures with colors varying from light green to dark green, were characterized by X-ray diffraction (Kristaloflex D5000, Cuk$\alpha$ with a Ni filter, and scanning rate of 2$^\circ$/min, in a range of 10-75$^\circ$). The pigments’ average crystallite size was calculated from X-ray line broadening ($d_{311}$) using Scherrer’s equation [16] and their morphology was investigated by scanning electronic microscopy (SEM). UV-vis-NIR spectroscopy (diffuse reflectance) was performed before and after firing of the pigments, using a Varian 5G spectrophotometer. In addition, the $L^*$, $a^*$ and $b^*$ color parameters and diffuse reflectance ofenameled samples were measured through the Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, in the 300-800 nm range, using D65 illumination. The CIE-$L^*a^*b^*$ colorimetric method recommended by the CIE (Commission Internationale de l’Eclairage) [17] was followed. In this method, $L^*$ is the lightness axis [$black (0) \rightarrow white (100)$], $b^*$ is the blue (-) $\rightarrow$ yellow (+) axis, and $a^*$ is the green (-) $\rightarrow$ red (+) axis.

**Results**

Fig. 1 shows the X-ray patterns of the powders derived from the $Zn01$, $Ni01$, $Cu01$ and $Co01$ compositions obtained by combustion reaction. The X-ray diffraction patterns indicate that the $MCr_2O_4$, ($M = Zn$, $Ni$, $Cu$, $Co$) compositions possessed well-defined diffraction peaks with a high degree of crystallinity. The $Ni01$ and $Co01$ compositions showed only the formation of single-phase normal crystalline spinel $MCr_2O_4$ ($M = Ni$ and $Co$). However, the $Zn01$ and $Cu01$ compositions revealed the presence of the normal primary crystalline spinel $MCr_2O_4$ phase ($M = Zn$ and $Cu$) and secondary $Cr_2O_3$ phase. The formation of the secondary $Cr_2O_3$ phase in the $Zn01$ and $Cu01$ compositions was attributed to the fact that the combustion flame temperature and time were insufficient for the complete formation of the normal spinel phase during the reaction. These parameters depend mainly on the intrinsic characteristics of each system and on the conditions under which the synthesis is performed [18]. According to Kiminami [11], the heating conditions affect the characteristics of the resulting powders. Moreover, both parameters directly affect the type
of agglomerate (soft or hard) and the particle size. Controlling these parameters during the synthesis is quite difficult, although they can be controlled through the specific control of the amount of fuel, the heating conditions (plate or muffle), the container type (Pirex-type becker, porcelain basin or vitreous silica basin) and the precursor type (nitrates, carbonates or acetates) used during the synthesis by combustion reaction [11].

![X-ray diffraction patterns of the MCr₂O₄ (M = Zn, Ni, Cu and Co) powders obtained by combustion reaction.](image)

Figure 1 – X-ray diffraction patterns of the MCr₂O₄ (M = Zn, Ni, Cu and Co) powders obtained by combustion reaction.

As reported by other researchers, the combustion flame temperature is decisive in the complete formation of the MCr₂O₄ phase. Thus, the fact that a Pirex-type becker was used as the receptacle for the reaction contributed directly to the presence of the secondary phase (Cr₂O₄) in the Zn01 and Cu01 compositions. The Pirex-type becker changed the kinetics and the exothermic nature of the reaction in a specific manner. The becker absorbs less heat from the external source (hot plate) needed to ignite the reaction; consequently, the combustion flame temperature of the reaction is reduced. The geometry of the Pirex-type becker also reduces the amount of oxygen required for synthesis. These two aspects strongly affect the powders’ final characteristics. In the case of the Ni01 and Co01 compositions, the temperature reached during ignition sufficed for the complete formation of the MCr₂O₄ (M = Ni and Co) spinel phase.

Figures 2, 3, 4 and 5 depict the powders’ morphologies obtained by scanning electronic microscopy (SEM) for, respectively, the Zn01, Ni01, Cu01 and Co01 compositions prepared by combustion reaction. The micrographs of all the compositions show the formation of soft agglomerates (sizes of around 10 to 20 µm) composed of particles whose smallest size is 200 nm. Fig. 2a shows the formation of soft agglomerates (easy deagglomeration, agglomerates held together by Van der Waals forces) with a porous and irregular morphology of quite fine particles. The micrograph in Fig. 2b shows particles with a morphology consisting of primary particles (without pre-sintering) and of secondary particles (with pre-sintering) in smaller intensity, with sizes inferior to 100 nm.

Fig. 3a reveals that the powder morphology of the Ni01 (NiCr₂O₄) composition was slightly less porous than the morphology of the Zn01 composition. However, it already presented the same aspects observed previously, i.e., formation of soft agglomerates with irregular morphology and sizes of less than 20 µm. Fig. 3b shows the particles’ size and morphology, revealing particles that are also quite fine (sizes under 150nm), with the formation of primary particles (without pre-sintering) and some particles displaying the beginning of pre-sintering (secondary particles). These results are slightly lower than the particle size observed for Zn01 composition. However, the particles were also found to be highly agglomerative.
Figure 2 – Micrographs obtained by SEM showing the morphology of the powder of the Zn01 (ZnCr$_2$O$_4$) composition resulting from the combustion reaction. (a) x 20K and (b) x 100K.

Figure 3 – Micrographs obtained by SEM showing the morphology of the powder of the Ni01 (NiCr$_2$O$_4$) composition resulting from the combustion reaction. (a) x 5K and (b) x 100K.

Fig. 4 shows the powder morphology of the Cu01 composition. Note that the soft agglomerates are also irregularly shaped and considerably porous, with sizes inferior to 20 µm. However, Fig. 4b reveals fine (size under 150 nm) and sufficiently agglomerated particles, i.e., many secondary particles (pre-sintering) were formed.

Figure 4 – Micrographs obtained by SEM showing the morphology of the powder of the Cu01 (CuCr$_2$O$_4$) composition resulting from the combustion reaction. a) x 5K, b) x 100K.

With regard to the Co01 composition, Figs. 5a and 5b indicate that the soft agglomerates formed were less porous than the agglomerates obtained with the Zn01 and Cu01 compositions. They were, however, very similar to the agglomerates formed in the Ni01 composition. The morphology observed here repeated the same aspects already found previously for the other compositions, i.e., irregular format and size under 20 µm. The particles were very fine, with sizes of less than 150 nm, though highly agglomerated.

Table 1 shows the crystallite size and average particle size of the Zn01, Ni01, Cu01 and Co01 powders. As can be seen, the crystallite size calculated using Scherrer’s equation [16] and the average particle size obtained by SEM ranged from 22.66 to 38.33 nm and from 76.5 to 111.28 nm, respectively. The powder of the Ni01 (NiCr$_2$O$_4$) composition resulted in the smallest crystallite size and smallest average particle size. In the Zn01 and Cu01 compositions, the crystallite sizes (32.16 and...
25.16 nm, respectively) were found to be inferior to those determined for the powder of the Co01 composition (38.33 nm). This difference was attributed to the presence of the second phase Cr₂O₃ revealed in the X-ray diffraction patterns. The differences in the average particle size and crystallite size were attributed to the combustion flame temperature, which differed for each composition and which is an intrinsic characteristic of each system.

Figure 5 – Micrographs obtained by MEV showing the morphology of the powder of the Co01 (CoCr₂O₄) composition resulting from the combustion reaction. a) x 20K, b) x 127K

Table 1 - Crystallites size and average particles size of the powders for Zn01, Ni01, Cu01 and Co01 compositions prepared by combustion reaction.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystallite Size (nm)</th>
<th>Average Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn01 (ZnCr₂O₄)</td>
<td>32.16</td>
<td>110.11 ± 49.69</td>
</tr>
<tr>
<td>Ni01 (NiCr₂O₄)</td>
<td>22.66</td>
<td>76.5 ± 15.29</td>
</tr>
<tr>
<td>Cu01 (CuCr₂O₄)</td>
<td>25.16</td>
<td>111.28 ± 33.87</td>
</tr>
<tr>
<td>Co01 (CoCr₂O₄)</td>
<td>38.33</td>
<td>99.2 ± 36.92</td>
</tr>
</tbody>
</table>

Fig. 6 shows the graphs of diffuse reflectance as a function of the wavelength for the powders of the compositions in question (Zn01, Ni01, Cu01 and Co01). Note that all the compositions displayed reflectance bands at around 400 nm (less intense) and 530 nm (more intense and highly defined in compositions Zn01, Ni01 and Co01), which correspond to the human eye’s visible region to stimulate the green color. The intensity of the diffuse reflectance band in the range of wavelength analyzed for the Cu01 composition was substantially inferior and slightly closer to 550 nm when compared with the other compositions. This was due to the greater proportion of secondary Cr₂O₃ phase observed in the X-ray diffraction patterns of this composition (Fig. 1), which caused the shade of green to change to a greenish olive shade (mud brown or ash brown).

Figure 6 – Values of diffuse reflectance as a function of the wavelength for the powders (unfired pigments) of the Zn01, Ni01, Cu01 and Co01 compositions obtained by combustion reaction.
In the case of the Zn01 composition, which also displayed the formation of secondary phase though in a lesser proportion than the Cu01, no substantial changes were observed in the band intensity of the analyzed wavelength band.

Fig. 7 shows the spectrum of diffuse reflectance as a function of the wavelength for the fired pigments (fired powders) of the Zn01, Ni01, Cu01 and Co01 compositions after application in the ceramic piece. The Zn01, Ni01 and Co01 compositions did not show significant alterations in the wavelength around 400 nm (less intense) and 530 nm (more intense), corresponding, for the human eye, to the stimulation of green color. The Zn01 composition, however, presented less intense diffuse reflectance bands in the two wavelength bands analyzed. This may have been a consequence of the secondary Cr$_2$O$_3$ phase observed in the X-ray diffraction patterns of the powder. The secondary Cr$_2$O$_3$ phase reacted, forming the completely crystalline ZnCr$_2$O$_4$ phase and altering the brilliant shade of green from light-green to a more intense light-green. In the Co01 composition that presented a larger quantity of the secondary Cr$_2$O$_3$ phase, a change was observed in the intensity of diffuse reflectance bands in the 400nm and 530nm wavelengths, which caused a change in the tone of the pigment color after application in the piece, shifting from mud brown (before application in the piece – unfired pigment) to a strong dark green shade (after application in the piece – fired pigment).

The color parameters ($L^*a^*b^*$) of the powders (unfired pigments) are given in Table 2. Note that replacing the metallic divalent Zn$^{2+}$ ions for Ni$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ ions caused the value of the parameter $L^*$ to decrease, which corresponded to a decrease in the lightness of the pigment, i.e., a darkening of the pigment’s color. Note, also, that the $a^*$ and $b^*$ parameters of the pigments of the Zn01 and Ni01 compositions remained in the same axis, i.e., axis $a^*$ negative and axis $b^*$ positive. However, the values of intensity were different, causing the shade of the pigment to shift from light to dark green. In the Cu01 composition, the $a^*$ and $b^*$ parameters were both positive, indicating that the color introduced a brown tone. The Co01 composition showed $a^*$ and $b^*$ parameters with negative coordinates, indicating a greenish-blue tone.

Table 2 - Coordinated $L^*a^*b^*$ of the Zn01, Ni01, Cu01 and Co01 composition before the application in the pieces (not fired pigment).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn01 (ZnCr$_2$O$_4$)</td>
<td>58,989</td>
<td>-0.537</td>
<td>9,740</td>
</tr>
<tr>
<td>Ni01 (NiCr$_2$O$_4$)</td>
<td>40,005</td>
<td>-5.950</td>
<td>6,096</td>
</tr>
<tr>
<td>Cu01 (CuCr$_2$O$_4$)</td>
<td>36,972</td>
<td>1,045</td>
<td>5,552</td>
</tr>
<tr>
<td>Co01 (CoCr$_2$O$_4$)</td>
<td>35,963</td>
<td>-11,656</td>
<td>-6,207</td>
</tr>
</tbody>
</table>
The color parameters ($L^*a^*b^*$) of the powders (fired pigments) after application in the ceramic pieces are given in Table 3. As can be seen, the replacement of the divalent Zn$^{2+}$ ions for Ni$^{2+}$, Cu$^{2+}$ and Co$^{3+}$ ions caused a reduction in the $L^*$ parameter, which corresponds to a decrease in the pigment’s lightness after firing. For the Zn01 and Ni01 compositions, after application of the pigment in the ceramic pieces, the $a^*$ and $b^*$ parameters were found to remain in the same axis, i.e., axis $a^*$ negative and axis $b^*$ positive, albeit with stronger intensities, indicating an alteration in the intensity of the pigments’ color from light bright green to a stronger less light green, in the case of the Zn01 composition, and from dark green to an intensely dark green, in that of the Ni01 composition. For the Cu01 composition, the most apparent change observed was in the $a^*$ parameter, which changed from the positive axis (before application in the piece – unfired pigment) to the negative axis (after application in the piece – fired pigment). The $b^*$ parameter remained positive, although its intensity increased. The change in the $a^*$ parameter led to a shift in the tone of the pigment’s color from brown (before application in the ceramic piece – unfired pigment) to dark green. In the Co01 composition, it was found that parameters $a^*$ and $b^*$ both resulted in coordinated negatives, though with a greater intensity. However, the reduction in the brightness observed in the $L^*$ parameter caused the tone of the color to change from greenish blue (petroleum green) to an intense bluish green.

A comparison of the values listed in Tables 2 and 3 with the diagram of solid colors illustrated in Fig. 8 reveals the changes in the pigments’ tones before and after application in the ceramic pieces. It can be observed that, generally, all the compositions showed a decrease in the $L^*$ factor, which represented a reduction in the lightness (darkening). The pigments of the Zn01, Ni01 and Co01 compositions, when applied in the ceramic pieces, showed increased $a^*$ and $b^*$ parameters, indicating that the pigments’ color did not change, but simply shifted to a more intense tone. The Cu01 composition showed a change in the $a^*$ parameter from positive to negative, while the $b^*$ parameter merely increased in intensity, resulting in a change of the pigment’s color from maroon to dark green.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn01 (ZnCr$_2$O$_4$)</td>
<td>41,254</td>
<td>-1,298</td>
<td>12,747</td>
</tr>
<tr>
<td>Ni01 (NiCr$_2$O$_4$)</td>
<td>18,850</td>
<td>-6,981</td>
<td>11,391</td>
</tr>
<tr>
<td>Cu01 (CuCr$_2$O$_4$)</td>
<td>28,495</td>
<td>-11,921</td>
<td>14,531</td>
</tr>
<tr>
<td>Co01 (CoCr$_2$O$_4$)</td>
<td>14,852</td>
<td>-29,856</td>
<td>-16,449</td>
</tr>
</tbody>
</table>

Figure 8 – Diagram of solid colors in $L^*$, $a^*$ and $b^*$
Summary

Combustion reaction proved to be an effective method of chemical synthesis for the preparation of ceramic oxide type spinel (M$\text{Cr}_2\text{O}_4$), with characteristics suitable for application as ceramic pigment. The powders (unfired pigments) displayed nanometric features, with crystallite sizes varying from 22.66 to 38.33 nm, ideal for optimal dispersion of the pigment during application in ceramic pieces. The X-ray diffraction patterns of the samples revealed lines of the secondary phase Cr$_2$O$_3$ "chromium oxide" in the Zn01 (ZnCr$_2$O$_4$) and Cu01 (CuCr$_2$O$_4$) compositions. The Ni01 and Co01 compositions showed only the single phase spinel MCr$_2$O$_4$ (M = Ni or Co). The use of several types of metallic ions allowed for different colored powders to be obtained, ranging from light green tones for the composition containing Zn, dark green for the composition containing Ni, olive green for the composition containing Cu, to a petroleum green tone for the composition containing Co. The curves of diffuse reflectance as a function of the wavelengths and the colorimeter coordinates of the Zn01, Ni01 and Co01 compositions after application in the ceramic pieces showed variations in the intensity of the color tones, although the same colors prevailed. In the case of the Cu01 (CuCr$_2$O$_4$) composition, a change was observed in the color as well as in the intensity of the tones due to the larger amount of secondary phase (Cr$_2$O$_3$).

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References