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Solution Combustion Synthesis of (Co,Fe)Cr_2O_4 pigments

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Abstract

The synthesis of mixed cobalt–iron chromites, $Fe_{1-\Psi}Co_{\Psi}Cr_2O_4$ ($0 \le \Psi \le 1$), has been studied by Solution Combustion Synthesis using urea as fuel. Characterization by XRD and SEM showed that crystallinity, cell parameters, crystallite size and grain size depend on Ψ. The higher is the cobalt content of the initial composition the greater are these four characteristics, but evolution of cell parameters, crystallite size and grain size is not regular, since the variations are more pronounced for the spinels with high iron content. Apparently, the method causes some deficiency in the oxygen content of the spinels and a slight enrichment in chromium with respect to the theoretical composition, but does not alter the proportions of iron and cobalt.

All synthesized chromites showed a high tinting strength in ceramic glazes without any additional annealing step.

Keywords: Powders-chemical preparation; Microstructure-final; Spinels; Colour; Pigment

1. Introduction

Spinels are one of the most numerous groups of ceramic pigments, since 16 of 44 pigments included in DCMA classification have this structure,[1] which has been widely described in literature.[2] Due to their industrial interest, many studies about spinels as ceramic pigments have been developed. Eppler studied the synthesis of numerous spinels by traditional ceramic method (involving solid state reactions between oxides at high temperatures for long times).[3–6] Later, other papers were published in the same way, as the one of Alarcón et al.[7] However, in the recent years researches have been aimed to other directions, being the synthesis of spinels by alternative methods one of the most important. These techniques have been applied to the synthesis of known spinel-type pigments as well as obtaining new spinels which can be also used as ceramic pigments.

New proposed methods have been focused on reducing the operation maximum temperatures and/or soak times, or obtaining pigments with controlled particle size. In this way, Pishch et al. synthesized $NiFe_2O_4$ and $CuCr_2O_4$ spinels from a mixture of their respective hydroxides obtained by coprecipitation.[8,9] Candeia et al. obtained $MgFe_2O_4$ ferrite, from a polymeric precursor (Pechini method).[10] Ouahdi et al. synthesized $CoAl_2O_4$ pigment by a reaction in molten salts.[11]

Solution Combustion Synthesis (SCS) is one of the most promising new methods, since it allows to synthesize the spinels with small particle size, using short reaction times and moderate temperatures.[12] The method begins by preparing an aqueous saturated solution with crystalline phase precursors in desired stoichiometry (nitrates are commonly used) and an adequate fuel (urea, glycine, hexamethylene tetraamine, etc.). Solution is heated quickly, so that water vaporised, generating a foamy raw material and finally the fuel ignition is produced, which provides necessary energy for the synthesis reaction. This method have been used to synthesize many mixed oxides by Patil group,[12] including numerous chromites,[13] being some of them classic ceramic pigments ($CoCr_2O_4$, $CuCr_2O_4$ and $FeCr_2O_4$). Following this method, Costa et al. obtained some ZnO–NiO–Fe_2O_3 ferrites.[14]

Despite the many materials synthesized by SCS, to our knowledge it has not been reported a systematic research about the spinels obtained when the divalent cation is progressively replaced for another, as well as characteristics and tinting strength of the products. This paper describes the synthesis of spinels of the system CoO–FeO–Cr_2O_3 by SCS, and their characterization from the mineralogical, microstructural and tinting strength, points of view.

2. Experimental procedure

$Fe_{1-\Psi}Co_{\Psi}Cr_2O_4$ ($0 \le \Psi \le 1$) pigments were prepared from the corresponding Fe, Co and Cr nitrates, urea and water. Urea

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proportion was calculated according to reaction stoichiometry to ensure the complete combustion of the mixture. As an example, to synthesize $Fe_{0.5}Co_{0.5}Cr_2O_4$ spinel, 20 g of $Fe(NO_3)_3{\cdot}9H_2O$ and 3.64 g de $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 25 mL of distilled water, then added 10 g of urea (all reagent were from Panreac Química, S.A.U., Spain). The mixture was placed in a pyrex container of 11 cm in diameter and 350 mL capacity which was introduced in a preheated kiln at 500 °C (BLF 1800, Carbolite Furnaces Ltd, UK). After 20 min of soaking time, the kiln was turned off and allowed to cool the sample. Other mixtures were prepared with the same method, varying the proportions of iron and cobalt, so Ψ covered the range from 0 to 1, in steps of 0.1.

Every pigment was wet milled in acetone in a ball mill, using agate jars to reduce the particle size (Pulverisette 5, Fritsch GmbH, Germany). The specific surface area was determined according to the BET method using the adsorption isotherm and nitrogen gas as adsorbent (Tristar 3000, Micromeritics, USA). The evolution of the crystalline phases present, the crystallite size and the cell parameters as a function of composition were monitored by XRD (Theta-Theta D8 Advance, Bruker, Germany), with CuKα radiation ($\lambda = 1.54183$ Å). The generator settings were 45 kV and 40 mA. The XRD data were collected in a 2θ of 5–90° with a step width of 0.015° and a counting time of 1.2 s/step by means of a VÅNTEC-1 detector. The collected data were used in a Rietveld refinement. The 4.2 version of the Rietveld analysis program DIFFRACplus TOPAS was used, assuming a pseudo-Voight function to describe peak shapes. The refinement protocol included the background, the scale factors and the global-instrument, lattice, profile and texture parameters. The microstructure of the samples was characterized by FEG-SEM (QUANTA 200F, FEI Co, USA), and its chemical composition determined by an energy-dispersive X-ray microanalysis instrument (Genesis 7000 SUTW, EDAX, USA).

Colour development was evaluated by introducing every pigment into a transparent single-fired tile glaze (2/98 wt% respectively) and subsequently fired in an electric laboratory kiln according to a thermal cycle of single-fired floor tiles (maximum temperature 1100 °C and 6 min hold at this temperature). The spectrophotometric curve and CIELab chromatic coordinates of the glazed surfaces were determined using CIE Illuminant D_{65} and CIE 10° standard observer (Color Eye 7000A, X-Rite Inc, USA).

3. Results and discussion

All the products of SCS reactions were a spongy mass, easy to disintegrate. Theirs colours changed from green-blue to dark brown, without any significant colour gradient inside, indicating that there had been no segregation of the different cations. Spongy structure of products are justified by the large volume of gases generated by combustion of urea ($CH_4N_2O + 3/2O_2 \rightarrow CO_2 + 2H_2O + N_2$), although Manoharan and Patil noted that this fuel favor sintering of formed particles, because the volume of gas generated is not sufficient to dissipate the heat of combustion quickly.[13] SEM analysis of obtained products confirmed this point, although it was observed a gradual evolution of microstructure in terms of the Co/Fe ratio in the initial mixture. The iron-rich chromites particles ($\Psi < 0.3$, Fig. 1) are composed of nanosized grains (maximum diameter about 50 nm) that had significantly sintered. By contrast, cobalt-rich chromites particles ($\Psi > 0.7$) had a slightly porous microstructure consisting also of nanosized grains, but better differentiated and with a size distribution shifted toward larger diameters (maximum diameter around 150 nm, Fig. 2). In line with the SEM images, the specific surface of the pigments decreased from 23 m^2/g to 20 m^2/g as Ψ increased from 0 to 1, confirming that the individual grains were sintered to form solids with low open porosity (an estimate of the specific surface for free spheres with the diameter of the individual grains of the pigments leads to values above 200 m^2/g).

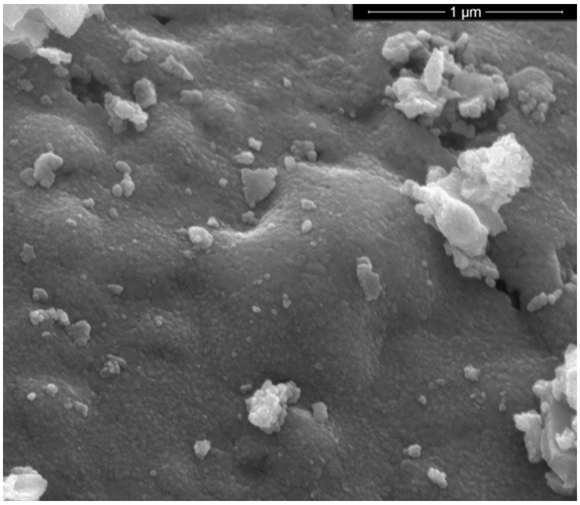

Fig. 1. Electron microscopy image of one particle of the pigment with $\Psi = 0$.

The chemical composition of the chromites measured by EDX (Fig. 3) showed an acceptable agreement between the atomic percentages of iron and cobalt with the mixtures of raw materials (the average deviation was −0.1% for Fe and +0.3 for Co, which are of the same order of the uncertainty of the technique). The behavior of chromium and oxygen was different,

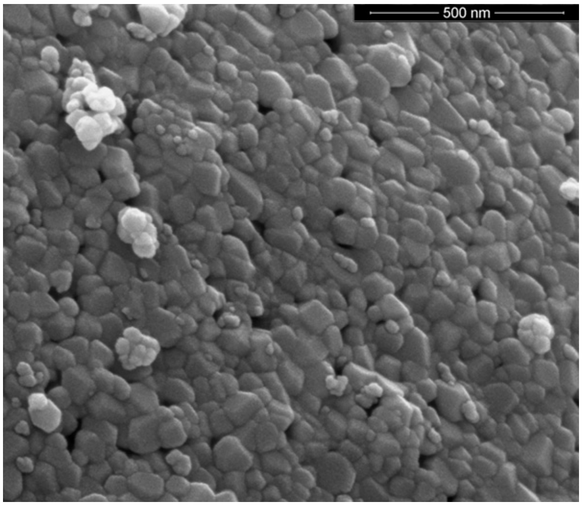

Fig. 2. Electron microscopy image of one particle of the pigment with $\Psi = 1$.

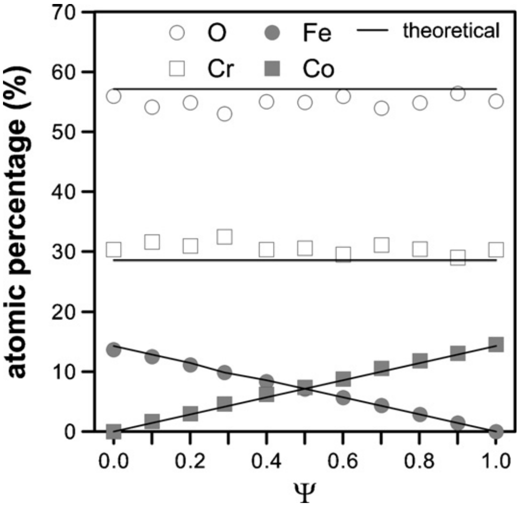

Fig. 3. EDX chemical analysis of the pigments, compared with the theoretical compositions.

because the atomic percentage of Cr was higher than expected in all the samples (the average deviation was +2.0%), and correspondingly the oxygen percentage was lower (−2.2% on average). As the atomic percentages of the elements showed no correlation with the crystallographic parameters of the spinels, it was concluded that the deviations were probably related with the synthesis method. The oxygen deficiency of the pigments could be explained considering the presence of the fuel during the SCS reaction, that may have promoted a reducing atmosphere. In addition, the fast kinetics impedes the equilibration of the oxygen content of the pigments after the crystallization of the lattice.

XRD analysis of synthesized samples showed a spinel-type main phase (Fig. 4), with reflections in positions within the ranges defined by the reflections corresponding to the $CoCr_2O_4$ and $FeCr_2O_4$. The eskolaite (Cr_2O_3) was detected as a minoritary phase in some samples, indicating that a fraction of chromium was not incorporated into the spinel structure. However, this fraction was very small and did not show any clear trend depending on the spinel composition. So that could be considered that the reaction was complete for practical purposes.

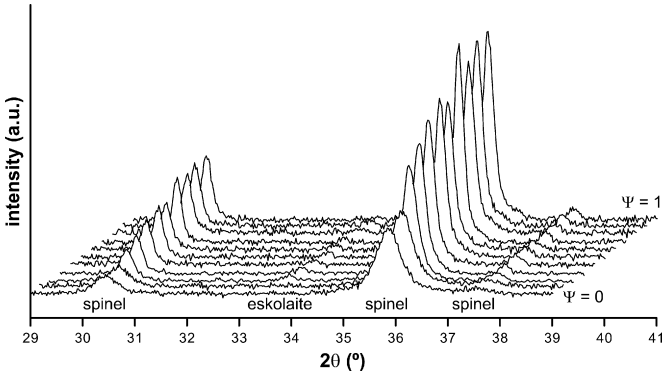

Fig. 4. Section of the XRD patterns of the pigments corresponding to the maximum reflection of spinel.

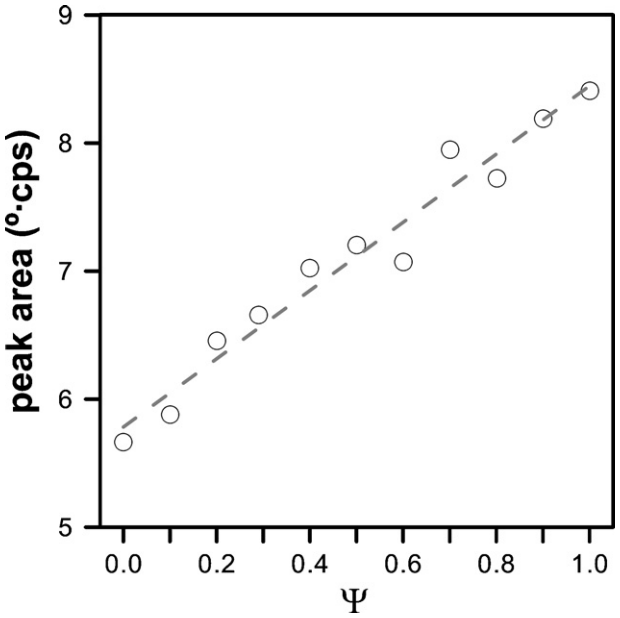

Fig. 5. Relationship between the area of I_{100} reflection of spinel and pigment composition.

The composition of the initial mixture exerted a pronounced effect on crystallinity, cell parameters and crystallite size of spinels. The mixture with $\Psi = 0$ (theoretically $FeCr_2O_4$), generated the chromite with the lowest crystallinity, and better crystallized spinels were obtained as the proportion of Co was increased, specifically the best crystallized chromite was obtained with $\Psi = 1$ composition (theoretically $CoCr_2O_4$). This is shown by the approximately linear trend in the I_{100} chromite reflection area as a function of Ψ (Fig. 5). The relation was more complex in the case of cell parameters, as they increased with Ψ without following a regular trend, because the variation was more pronounced in the pigments with $0.2 \leq \Psi \leq 0.8$, and less marked for the pigments with $\Psi < 0.2$ or $\Psi > 0.8$ (Fig. 6). The general trend of the lattice parameters of the cell was

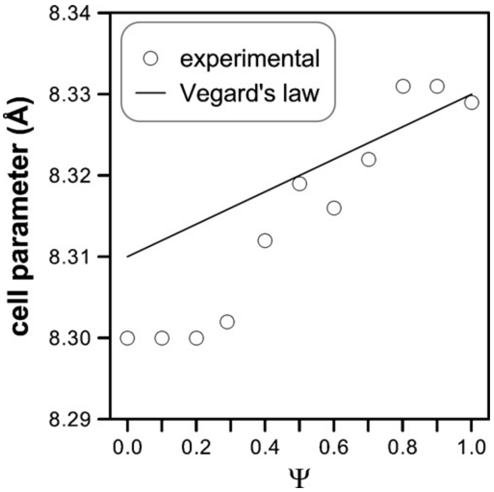

Fig. 6. Comparison of cell parameters of the spinel with the prediction of Vegard's law, based on the ICCD data from the spinels $FeCr_2O_4$ ($\Psi = 0$) and $CoCr_2O_4$ ($\Psi = 1$).

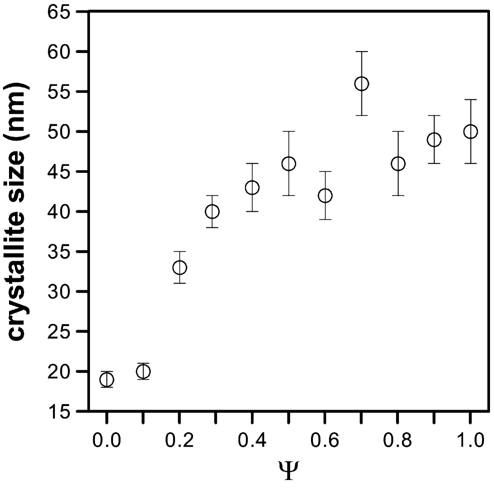

Fig. 7. Relationship between the crystallite size of spinel and pigment composition.

consistent with the greater ionic radius of Co^{2+} with respect to Fe^{2+}. However the lattice parameters of the iron-rich pigments were lower than the reported values (8.310 Å for the $FeCr_2O_4$[15] and 8.329 Å for the $CoCr_2O_4$[16]), and the evolution was less regular as expected according to the Vegard's law (as in the results of de Souza et al. in the $Co_xZn_{1-x}Al_2O_4$ system[17]). Thus it was concluded that the fast reaction kinetics of SCS method make difficult reaching the equilibrium structure of the spinels, specially for high iron contents ($\Psi < 0.5$). The crystallite size of the pigments showed a trend similar to cell parameters (Fig. 7). The smaller crystallites were measured in the iron-rich pigments, and the bigger in the cobalt-rich pigments, but the variation was more pronounced for $\Psi < 0.5$, corroborating the negative effect of iron over the crystallization of the spinel. Comparing the results of XRD and microscopy, it follows that the grains are composed of several crystallites, since grain size is about three times that of the crystallites.

The absence of a pattern in the presence of Cr_2O_3 as a minoritary phase in some samples and the variability detected in the I_{100} reflection area, crystallite size and cell parameters, indicates that SCS may not have enough reproducibility in the characteristics of the product generated, but this features could be improved with a subsequent thermal treatment.

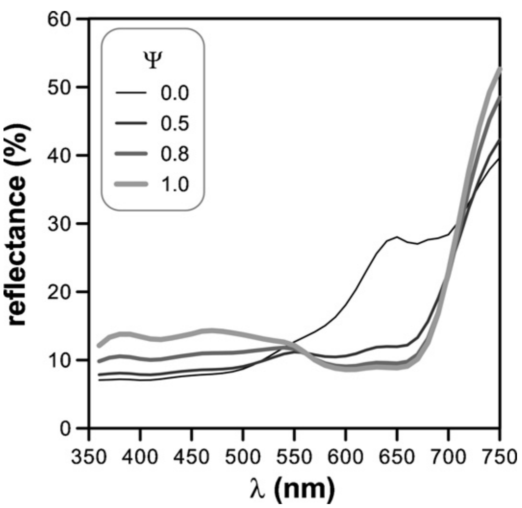

Fig. 8. Spectrophotometric curves of the glazes that incorporated four of the synthesized pigments.

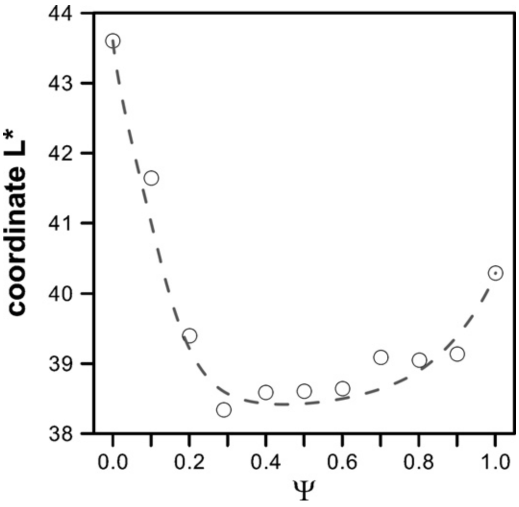

Fig. 9. Relationship between the L^* coordinate of the glazes and pigment composition.

The incorporation of the eleven samples into a transparent glaze generated intense coloured surfaces in all cases. This confirmed that all synthesized chromites behave as ceramic pigments, despite their particles were formed by nanosized grains. Colour palette obtained covers from reddish brown ($\Psi = 0$) to blue-green ($\Psi = 1$), through relatively pure but little saturated green and yellow ($\Psi = 0.8$ and $\Psi = 0.5$ respectively). In the glaze reflectance curves (Fig. 8), it was observed that when Fe is replaced by Co, the characteristic absorption band of Co(II) in tetrahedral position (occurring between 570 and 700 nm) gradually increases its intensity.[7]

The evolution CIELab coordinates exhibited a strong correlation with the spinel composition. L^* showed the most complex evolution, but within a narrow range of variation

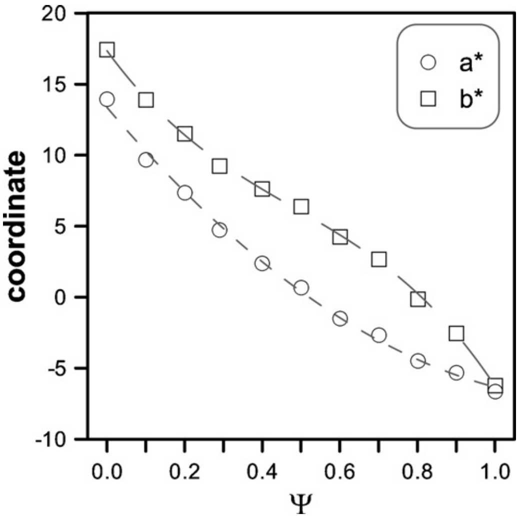

Fig. 10. Relationship between a^* and b^* coordinates of the glazes and pigment composition.

(Fig. 9). Specifically L^* presents a minimum for $\Psi = 0.3$, although pigments with lower values of Ψ generated quite bright colours, while pigments with higher values showed a much more moderate upward trend. a^* and b^* coordinates exhibited a downward trend depending on Ψ (Fig. 10), although the trend is slightly parabolic in the case of a^*, while b^* has a slight sigmoidal path. It is likely that such marked changes in the brightness of the colours generated by iron-rich chromites, are due in part to their lower crystallinity, as this would facilitate the attack by the molten glaze generated during firing. Even in these conditions, the tinting strength of these chromites is remarkable, and possibly could be improved by subsequent heat treatment, which would enhance the crystallinity and increase grain size.

4. Conclusions

It has been shown that the Solution Combustion Synthesis allows to obtain mixed chromites ($\mathrm{Fe}_{1-\Psi}\mathrm{Co}_{\Psi}\mathrm{Cr}_2\mathrm{O}_4$ with $0 \leq \Psi \leq 1$) using urea as fuel. The process is very fast and chromites are obtained as a spongy mass that disintegrates easily. SCS causes a slight deficiency of oxygen in the chromites which is independent of the composition, and is not reflected in the crystal structure. The composition of the mixture of raw materials has a very significant effect on the spinel cell parameters, crystallinity, crystallite size and grain size. The higher is the cobalt content better crystallized chromites are obtained, with higher crystallite and grain size. Iron-rich chromites are those with more pronounced changes in cell parameters and crystallite size. The effect of the composition is also detected in the microstructure of the particles, consisting of sintered nanosized grains. By increasing the iron content the grains are more sintered and their size is smaller.

All chromites exhibit a high tinting strength in a transparent glaze without any additional thermal treatment, covering a fairly broad colour palette.

Acknowledgements

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