COLOUR GAMUT OF SPINELS OBTAINED BY SOLUTION COMBUSTION

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1. INTRODUCTION

Spinels are one of the most important groups of ceramic pigments owing to the versatility of their structure in accommodating different chromophore cations. Just as other pigments, spinels are synthesised industrially using the traditional ceramic procedure, which entails very high energy consumption because of the high temperatures and long thermal treatment time required.

Solution combustion synthesis constitutes an alternative to the traditional procedure1 because it allows spinels to be directly obtained from an aqueous solution that contains a combustible material and the spinel precursors, operating at moderate temperatures (<600ºC) and times of the order of minutes.

The study evaluated the feasibility of synthesising a large group of spinels, combining trivalent cations (Fe^{3+}, Cr^{3+}, and Al^{3+}) with divalent cations (selected among Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+}), according to the trivalent cation.

2. EXPERIMENTAL PROCEDURE

The raw materials used to synthesise the different spinels were the nitrates of the elements contained in the spinel composition, whereas the combustible material was urea (all supplied by Panreac).

The preparation of the aqueous solutions of raw materials, the combustion conditions, and the treatment of the obtained product have been described elsewhere.[2]

The crystal structures were identified by X-ray diffraction of the powder sample, using a BRUKER Theta-Theta model D8 Advance diffractometer. Colouring strength was evaluated by incorporating each pigment into a transparent single-fire glaze, in a proportion of 2/98 by weight. After firing according to a standard floor tile cycle (T_{max}=1110ºC), the CIELab chromatic coordinates were determined with a Macbeth Color-Eye7000A spectrophotometer (D_{65} and 10º).

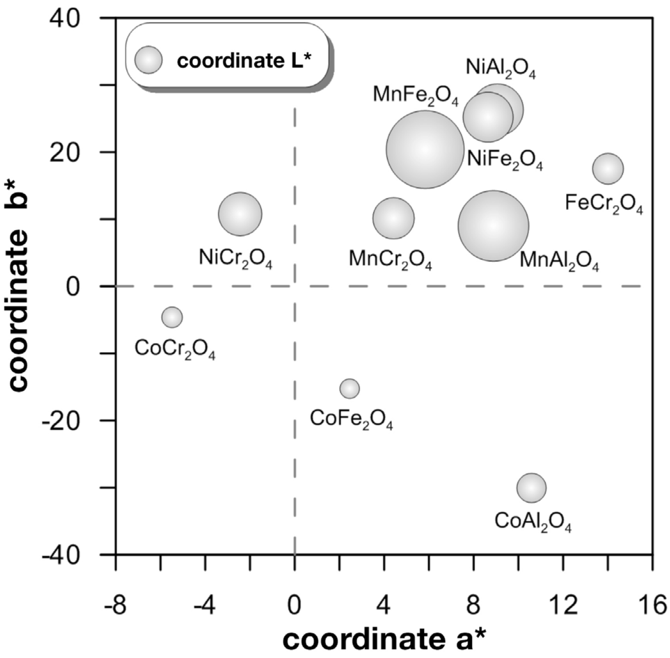
3. RESULTS

A group of 13 spinels were synthesised, in each case obtaining very sponge-like masses that readily disaggregated. The mineralogical characterisation indicated that three of the compositions had not generated the expected phase. The other ten had principally generated the desired phase, albeit with different degrees of crystallinity (see table with the XRD analysis results). The chromites appeared to be the spinels with the greatest tendency to crystallise during combustion synthesis, whereas the ferrites and aluminates exhibited greater difficulties, particularly when cations were involved that could be incorporated into the lattice with different degrees of oxidation.

OBJETIVE	MAJOR PHASE	MINOR PHASES	CRYSTALLINITY
$CoCr_2O_4$	Cochromite ($CoCr_2O_4$)	-	low
$MnCr_2O_4$	Manganochromite ($MnCr_2O_4$)	-	high
$NiCr_2O_4$	Nichromite ($NiCr_2O_4$)	Eskolaite (Cr_2O_3)	high
$FeCr_2O_4$	Chromite ($FeCr_2O_4$)	-	low
$CuCr_2O_4$	Eskolaite (Cr_2O_3)	Tenorite (CuO), mcconellite ($CuCrO_2$)	-
$CoFe_2O_4$	Spinel ($CoFe_2O_4$)	Cobalt oxide (Co_3O_4)	low
$MnFe_2O_4$	Jacobsite ($MnFe_2O_4$)	Hematite (Fe_3O_4), hausmannite (Mn_3O_4),	low
$NiFe_2O_4$	Trevorite ($NiFe_2O_4$)	Hematite (Fe_2O_3)	very low
$ZnFe_2O_4$	Zincite (ZnO)	Hematite (Fe_2O_3)	-
$CoAl_2O_4$	Spinel ($CoAl_2O_4$)	-	very low
$MnAl_2O_4$	Galaxite ($MnAl_2O_4$)	-	low
$NiAl_2O_4$	Spinel ($NiAl_2O_4$)	Bunsenite (NiO), gibbsite ($Al_2O_3 \cdot 3H_2O$)	low
$FeAl_2O_4$	Magnetite (Fe_3O_4)	Hercynite ($FeAl_2O_4$)	-

The colouring strength evaluation of the ten samples that consisted mainly of spinel produced a colour palette that encompassed different bluish and greenish tones, as well as a wide range of browns (see figure).

The results showed that it was possible to synthesise, at a lower cost in time and energy, a great number of spinels by combustion of a judiciously formulated solution. These spinels had a high colouring strength, in addition to a very sponge-like morphology, which would facilitate subsequent milling to reduce particle size to inkjet technology requirements.



Chromatic coordinates generated in the fired glaze.

4. ACKNOWLEDGEMENTS

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