THEORETICAL/EXPERIMENTAL STUDY OF IRON-DOPED ALUMINA PIGMENTS

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Most pigments consist of substances that have a specific crystalline structure. Generally speaking, a pigment consists structurally of a host lattice, in which the pigmenting component is integrated, i.e. the chromophore, (normally a transition cation or internal transition) and the possible stabilizing and modifying components, which contribute to or strengthen the pigmenting properties (pigmenting strength and colour tone). In the present study, alumina-iron pigments were synthesized, with a view to analyzing the role of the iron ion in the alumina matrix. To obtain the powders, the polymer precursor method was used, with the addition of iron ions by moles (2, 4 and 8%). The powders were first precalcined at 350°C for thirty minutes, then completing calcining at temperatures in the range between 700° and 1100°C, for 2.5 hours.

The crystallographic evolution of *gamma* and *alpha* alumina was monitored by X-ray diffraction (Figure 1), which showed the existence of a more stable phase (*corundum*) for the powders calcined at a temperature of 1100°C. It was observed that the iron ion accelerated the alumina phase transition.

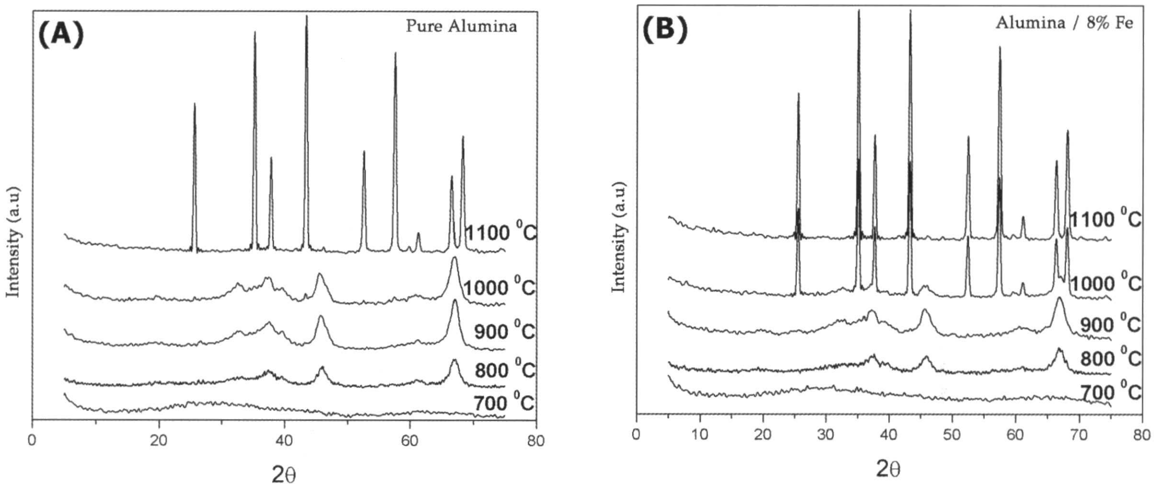

Figure 1. X-ray diffractograms (A) pure alumina (B) alumina doped with 8 mol% iron.

No vibrational modes were noted by Raman spectroscopy for the pigments calcined at 900°C, which showed the cubic geometry of the γ-alumina obtained at this temperature. However, peaks were observed, around 480 and 810 cm^{-1} relating to Fe-O stretching and in the 400 and 700 cm^{-1} regions relating to Al-O, characterizing the rhombohedrai geometry of α-alumina formed at 1000°C. UV-visible spectroscopy (Figure 2) confirmed a band at 460 nm which characterizes the yellow colour of the pigments, relating to the transition $^6A_1 \rightarrow 4A_{1g}, ^4E_g$, and at 1100°C four other possible transitions of Fe^{3+} (d^5) were observed.

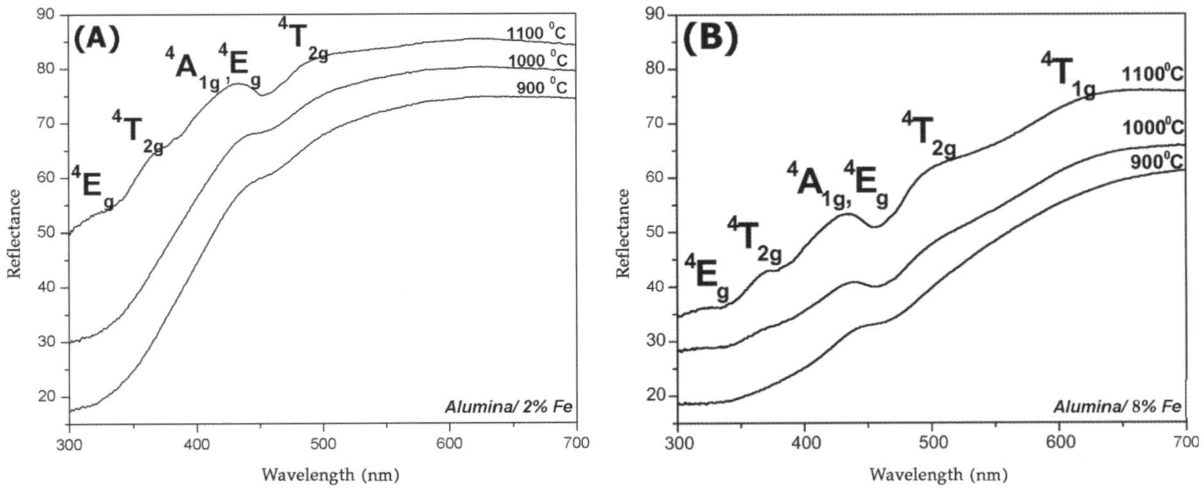

Figure 2. Reflectance spectra of the pigments (A) 2 mol% iron (B) 8 mol% iron.

Analysis of the colorimetric coordinates confirmed a variation of the yellow intensity of the pigments and the linear behaviour of the chromatic coordinates (L, a*, b*) in relation to dopant concentration and the increase in temperature.

Transmission electron microscopy showed the existence of nanoparticles with a size ranging from 7 to 11 nm, for the *gamma* phase at 900°C (Figure 3A), and the material is found in monocrystalline form with particles larger than 100 nm at 1100°C (Figure 3B).

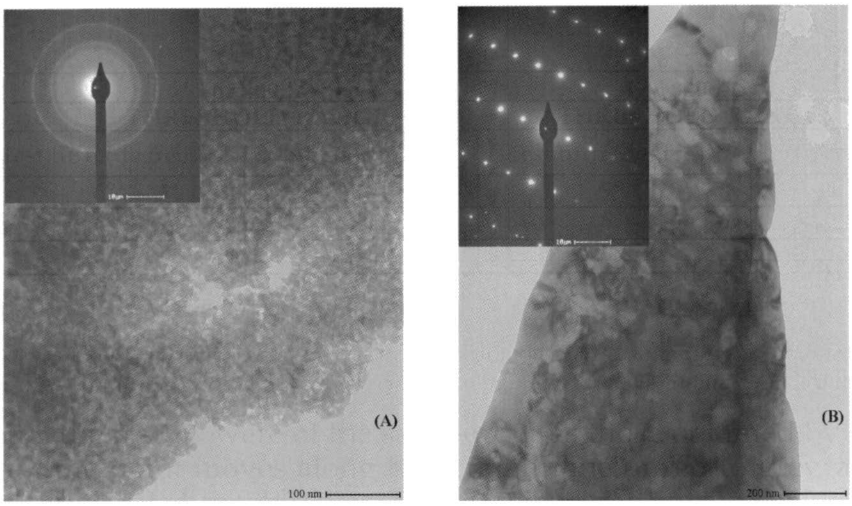

Figure 3. Micrographs obtained through TEM of pigments (A) 2 mol% iron (B) 8 mol% iron.

A quantum mechanical study of the *gamma* alumina phase was also conducted with a view to clarifying the experimental results obtained. The γ-alumina crystallizes in a spinel structure and has a space group; the most frequently attributed is FD3M with a=7.911 Å, which corresponds to the formulation Al_2O_4 detailed in Table 1.

ATOM	SITE	X	Y	Z
Al	8a	0.5	0.5	0.5
Al	16d	0.125	0.125	0.125
O	32e	0.225	0.225	0.225

Table 1. Atomic positions of γ-alumina.

In order to obtain the Al_2O_3 stoichiometry, the primitive cell was used with a=b=c=5.594 Å and $\alpha=\beta=\gamma=60°$ which contains 14 atoms (Al_6O_8). The cell was then multiplied by 3 ($Al_{18}O_{24}$) and two atoms of Al were eliminated, thus obtaining $Al_{16}O_{24}$. The vacancies are preferentially at the octahedral sites[1], so as to leave a more stable structure. Figure 4 displays 3 primitive cells indicating the positions of the vacancies.

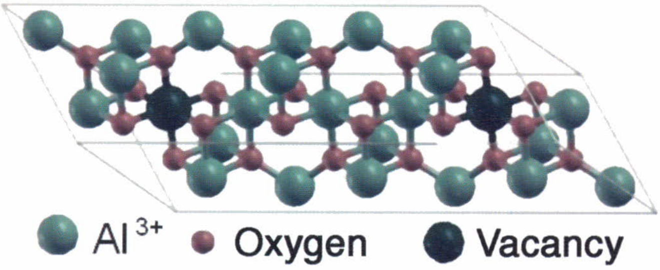

Figure 4. Model of the γ-alumina structure.

The structure and atomic positions were optimized in the VASP program, a program of ab initio molecular dynamics. Two optimization attempts were run. In the first, maintaining a fixed geometry, the optimized parameters of the primitive cell were 5.5769 Å. For the second, with the free program, the parameters obtained were a=b=5.5794 Å, c=5.4618 Å and $\alpha=\beta=60.002°$ and $\gamma = 59.998°$.

REFERENCES

[1] GUTIERREZ, G., TAGA, A., JOHANSSON, B., "Theoretical structure determination of g-Al2O3" Physical Review B, 65:012101, 2001.