CERAMIC PIGMENTS BASED ON ARMALCOLITE DOPED WITH VANADIUM BY MOD METHODS

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1. INTRODUCTION

Armalcolite is the structure (orthorhombic, point group 2/m2/m2/m and space group Bbmm) of a mineral detected for the first time in rocks brought from the first lunar exploration in 1969; the name comes from the first letters of the astronauts of this first moon expedition (1): ARMstrong, Aldrin and COLlins. Its stoichiometry and oxidation state vary between the extremes $(Mg_{0,5}Fe_{0,5})Ti_2O_5$ (detected in lunar rocks) and ferroarmalcolite (armalcolite, ferrian) $(MgFe)(FeTi_3)O_{10}$ with Fe(II) in the former case and Fe(III) in the latter. Synthetically, it is obtained by calcination at high temperature followed by drastic quenching. If it does not metastabilise by quenching, it breaks down into Mg-ilmenite ($Mg\text{-}FeTiO_3$) and rutile. This study examined the possible use of armalcolite stabilised by doping with vanadium $(Mg_{0,5}Fe_{0,5})(V_xTi_{2-x})_5O_5$ as a ceramic pigment.

2. EXPERIMENTAL AND RESULTS

$Mg_{0.5}Fe_{0.5}(V_xTi_{2-x})_2O_5$ samples were prepared by the CE route (Ceramic from $Mg_2(OH)_2CO_3$, iron oxide (III), anatase and NH_4VO_3), CO (ammoniacal coprecipitation of a solution with NH_4VO_3 dissolved in nitric acid, $Mg_2(OH)_2CO_3$, $Fe(NO_3)_3.9H_2O$ and titanium isopropoxide stabilised with acetylacetone) and by the MOD route (metal organic decomposition with additions of a polycarboxylic acid in an oxalic/citric molar ratio: sum of cations = 0 0.25 1 1.5 and 2) (2). The powders were successively calcined at 500ºC/1h and 1000ºC/3h, and they were characterised by X-ray diffraction (Figure 1), glazed in double-firing and monoporosa frits (Fig. 2), and by scanning electron microscopy SEM (Fig. 3), measurement of the BET specific surface area, and diffuse reflectance spectroscopy (Fig. 3).

3. CONCLUSIONS

Operating by the ceramic route, the powders calcined at 1000ºC/3h crystallised ferroarmalcolite as major phase together with rutile. These powders develop blue colorations (L*a**b*=66/-0.5/-2.3) with double-firing glazes (1050ºC) associated with V(IV) (Fig. 3), which become greenish (L*a*b*= 71.5/-0.2/13.9) in monoporosa glazes (1080ºC). From x=0.1 X-ray diffraction indicates the generation of magnesium vanadates such as $Mg_3(VO_4)_2$. The use of ammoniacal coprecipitation routes and MOD (metal organic decomposition) (2), by means of chelation with oxalic or citric acids in different molar ratios, produce crystallisation of ferroarmalcolite with treatments of only 500ºC/1h. At 1000ºC, rutile is detected together with ferroarmalcolite (Fig. 1). The resulting colorations intensified in the MOD samples, although it was not possible to stabilise the blue colorations in the monoporosa glazes (Fig. 2).

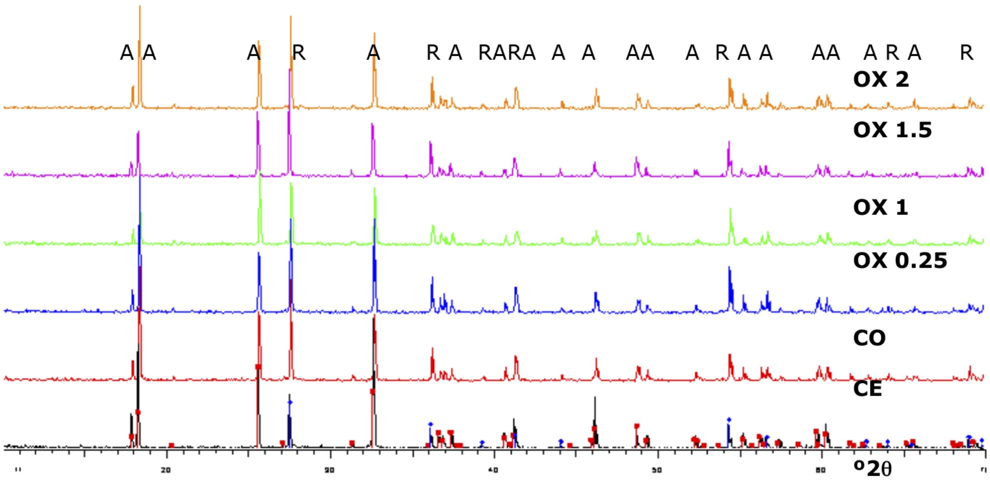
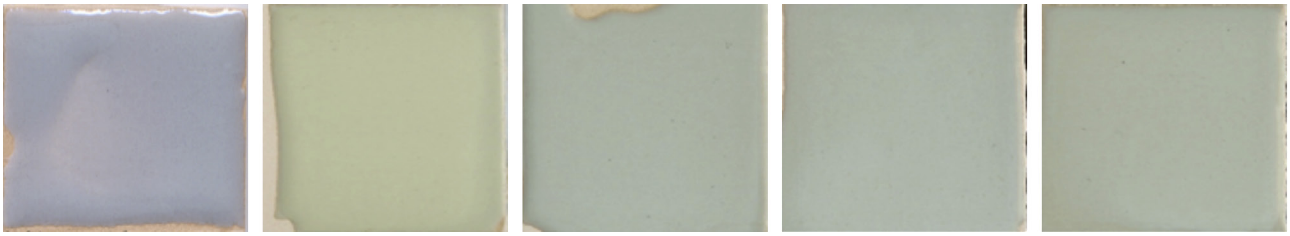


Figure 1. X-ray diffraction (A=Armalcolite (MgFe)(FeTi$_3$)O$_{10}$, R=Rutile TiO$_2$).



CE Double firing 66/-0,5/-2,3

CE Monoporosa 71.5/-0.2/13.9

CO Monoporosa 67.1/-0.7/4.8

CIT 0,25 Monoporosa 69.3/-1.0/4.4

OX 1,5 Monoporosa 66.5/-0.2/6.0

*Figure 2. Glazed tiles and CIEL*a*b* values.*

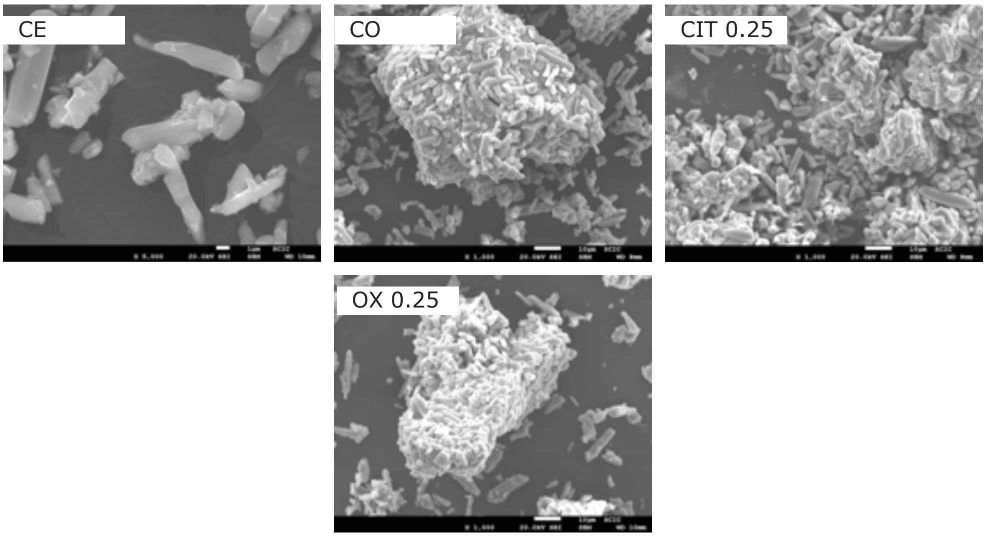


Figure 3. SEM micrographs.

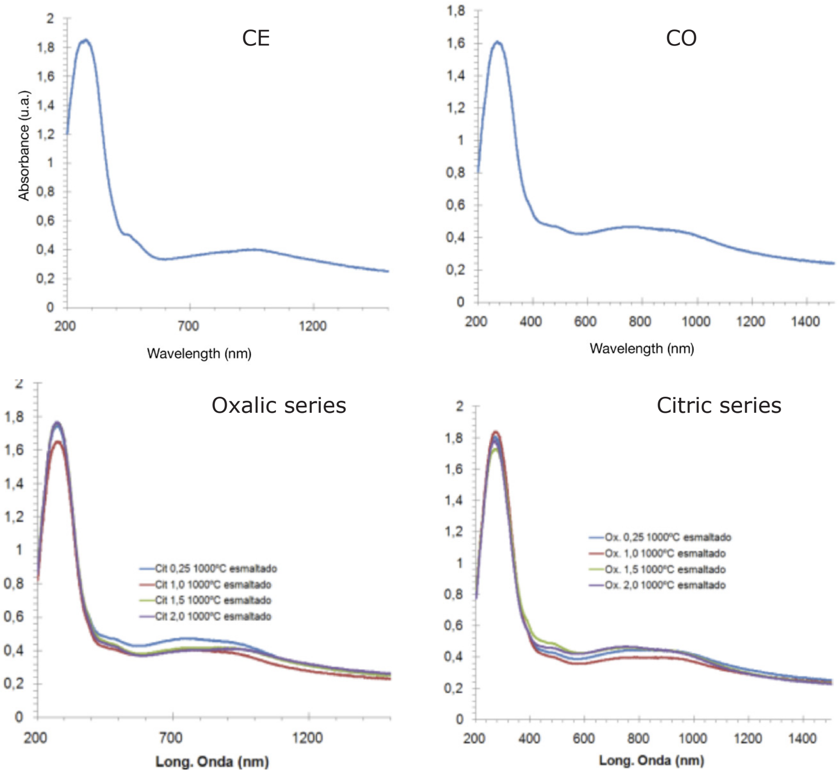


Figure 4. Diffuse reflectance spectra of the monoporosa glazings.

4. ACKNOWLEDGEMENTS

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