THE DUAL ROLE OF V_2O_5 IN PRODUCING THE TURQUOISE BLUE COLOUR OF VANADIUM-DOPED ZIRCONIUM

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1. INTRODUCTION

The production of ceramic pigments by the traditional method is based on solid state reactions[1,2], whereby crystalline phases having the characteristics required of a pigment are obtained. However, the low reactivity of the raw materials used in these pigments leads to low yields and high production costs, thus making it necessary to raise firing temperatures. A common practice is to use mineralizers to hasten the reaction kinetics, thereby lowering the firing temperature. In this context, we examined the dual role of vanadium pentoxide as a chromophore and a mineralizing agent. To this end, we formulated compositions containing equal molar amounts of silica and zirconium (ZrO_2-SiO_2), a varying vanadium content (4, 7 and 10% of V_2O_5), and a fixed amount of mineralizer. The samples were calcined at temperatures of 900, 1000 and 1100ºC for 3 hours, ground in a mortar, milled, washed and dried. XRD and XANES analyses evidenced the action of V_2O_5 as a mineralizer in the liquid phase. Our colorimetric results indicated that the colour was directly dependent on the dopant content.

2. MATERIALS AND METHODS

The raw materials were weighed on an analytical scale with a confidence level of ± 0.001g, in equal molar proportions (1:1), representing 33% in mass of SiO_2 and 67% of ZrO_2. A mineralizer and three different V_2O_5 contents, i.e., 4%, 7% and 10%, were added to the composition, thus constituting three distinct formulations, which were mixed by the dry ball milling technique. The mixtures were heat-treated at 900, 1000 and 1100°C for 1 hour in an EDGCON 5P electric furnace. The calcined samples were then ground in a mortar and a fraction of each composition was separated for mineralogical analysis by XRD, using CuKα radiation, with 2θ from 18° to 40°, 0.5°/min (Siemens D5005). The purpose of this analysis was to identify the crystalline phases formed during the various stages of the reaction. After calcination and analysis, the samples were milled in a ball mill containing 50% water and 8% NaOH, down to a residue of 0% in #325, then washed three times (in 1 litre of water each time) and oven-dried. The pigments were incorporated in the proportion of 5% into a standard transparent enamel and a 0.5mm thick layer was applied with a binil on industrial BIIb engobed floor tiles. The floor tiles were fired in an industrial furnace in a 30-min cycle at a threshold temperature of 1140°C, and then subjected to colorimetry tests (Minolta 2500d with D65 illuminant).

3. RESULTS AND DISCUSSION

3.1. X RAY DIFFRACTION

Figure 1 shows the diffractograms at 900 and 1000°C for 1 hour, comparing the influence of the vanadium pentoxide contents of 4%, 7% and 10% in the mixture on the zirconium silicate formation reaction. Note that the sample containing 4% of V_2O_5 does not present the formation of the phase of interest, while the other two samples containing V_2O_5 contents of 7% and 10%, respectively, display peaks corresponding to zirconium silicate phase. The results indicate that V_2O_5 acts as a mineralizer, accelerating the reaction kinetics through two kinetic mechanisms acting jointly: 1) formation of liquid and/or vapour phase at low temperatures, facilitating and increasing mass transport in the ion diffusion, and 2) formation of the most reactive intermediary stages. Results such as these were reported by Monrós[3], who observed the same behaviour of the V^{+4} ion in the production of vanadium-doped zirconium silicate turquoise blue ceramic pigment.

Figure 1. DRX comparing the influence of the vanadium pentoxide contents of 4%, 7% and 10% at a) 900 and b) 1000°C for 1 hour

Other mechanisms have been proposed for V_2O_5 to act in reducing the zirconium silicate formation energy. Matkovitch and Cobert[4] suggested that, at around 690°C, vanadium acts by forming zirconium pyrovanadate (ZrV_2O_7) as a reactive intermediary in the absence of mineralizers, decomposing at around 760°C to form zirconite.

3.2. X RAY ABSORPTION NEAR-EDGE STRUCTURE

Figure 2. XANES spectra of the samples containing 4% of V2O5 dopant calcined at 900, 1000 and 1100°C for 1 hour

Figure 2 shows the XANES spectra of the samples containing 4% of V_2O_5 dopant calcined at 900, 1000 and 1100°C for 1 hour compared with two patterns with different vanadium oxidation states: V_2O_5 (5+) and $VOSO_4$ (4+), and a highlighted magnified view of the region of the main peak.

Note the well-defined peak at 5.47 keV with energies corresponding to V_2O_5 (V^{5+}) shifting slightly to energies corresponding to $VOSO_4$ (V^{4+}), indicating a change in the oxidation state of the chromophore ion. This result reinforces the data in the literature ascribing the blue colour of the pigment under study to the V^{4+} ion[5,6].

An analysis of the region with the highest energies (between 5.48 and 5.53 keV) reveals a poorly defined region (called a structurally disordered region) in the samples calcined at 900 and 1000°C for 1 hour, which is not visible in the sample calcined at 1100°C for 1 hour. This disorder may originate from the amorphization of vanadium pentoxide during firing due to the effect of its fusion. At this stage, the dopant is still outside the host crystal, but this leads to the hypothesis that it has already reached the 4+ oxidation state, which is characterized by the shift of the peak in the region of 5.47 keV.

3.3. COLORIMETRIC ANALYSIS

Shown below are the results of the influence of temperature and dopant content on parameter b* (summarizing: b*<0: blue and b*>0: yellow). Figure 3 illustrates the CIELab colorimetric space.

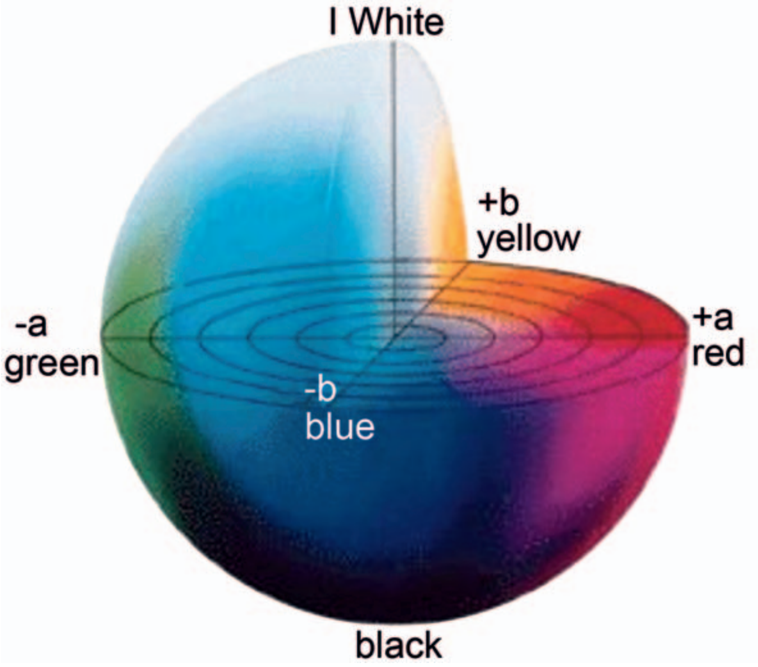


Figure 3. CIELab colorimetric space

Figure 4 shows the colorimetric results represented by the b* parameter, highlighting the influence of the dopant content on the colour.

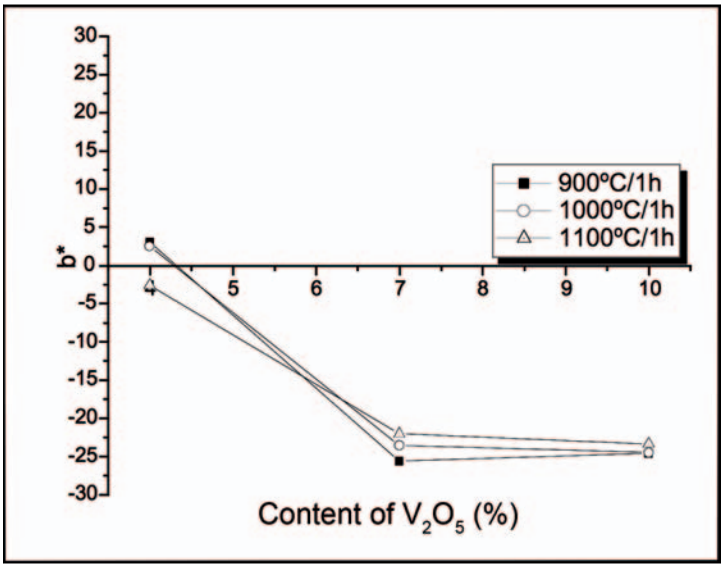
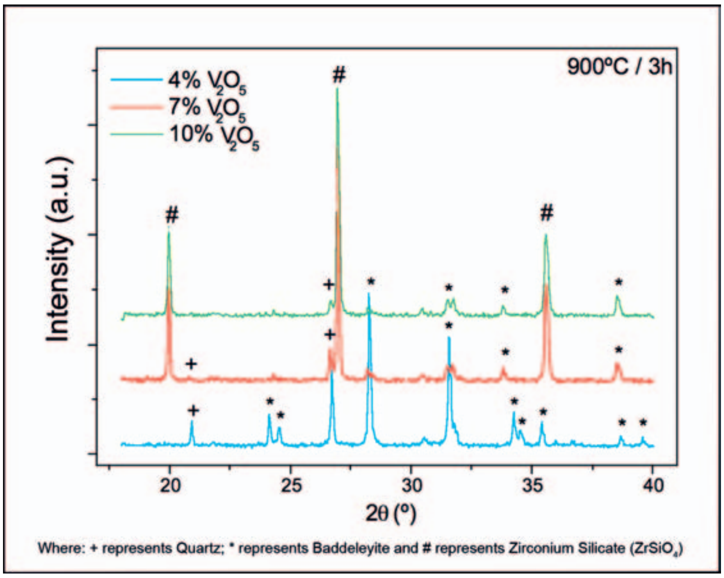


Figure 4. Colorimetric results represented by the b parameter for contents of 4%, 7% and 10%*

The results indicate the influence exerted by the dopant content on parameter b*. Note the sharp drop when the content increases from 4 to 7%, remaining reasonably constant up to 10%. This decrease in the value of b* indicates a greater incorporation of the blue component in the colour developed by the pigment, i.e., the pigment becomes "bluer" when the dopant content increases from 4 to 7%, remaining constant up to 10% of V_2O_5.



Where: + represents Quartz; * represents Baddeleyite and # represents Zirconium Silicate ($ZrSiO_4$)

Figure 5.

At the values used in this study, this stabilization from 7% on indicates that 7% represents the vanadium saturation limit in the host zirconium silicate crystal. Thus, any additional percentage of V_2O_5 is not effectively converted into ions inside the matrix, and is removed in the basic leaching process. It is worth keeping in mind that, according to J. D. Lee[7], V_2O_5 is highly soluble in the concentrated sodium hydroxide used in the leaching process.

4. CONCLUSIONS

After carrying out the above described methodology, the following can be concluded: 1) XRD revealed that V_2O_5 acts as an accelerating agent, or mineralizer, of the reaction kinetics. 2) Our colorimetric results indicate that V_2O_5 acts as a colour-forming agent, with saturation of the $ZrSiO_4$ host crystal occurring from a 7% content up. 3) The XANES results indicate that V_2O_5 acts by forming liquid phase and accelerating the reaction kinetics, and that the blue colour derives from the +4 oxidation state of vanadium.

5. ACKNOWLEDGEMENTS

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