GLAZE-COLOUR REACTIVE INTERACTION OUTGASSING CONTROL WITH CERIANITE-BASED PIGMENTS

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1. INTRODUCTION

Several rare-earth oxides and transition metals present variable oxidation states, developing sesquioxides and non-stoichiometric oxides; this is the case of the development of Co_3O_4 spinels, with the presence of Co^{3+} and Co^{2+} in pigments that use cobalt in their composition [1] and more recently in the use of cerianite-based pigments doped with other rare earths [2].

CeO_2 is the only oxide with a fluorite LnO_2 structure that can be produced in a stoichiometric way by reaction between molecular oxygen and cerium (III) oxide. The other two well-known oxides with this stoichiometry, PrO_2 and TbO_2, are only obtained either under pressure with oxygen (PrO_2) or with atomic oxygen (TbO_2) (3). The three oxide systems present a complex phase diagram, with the formation of different intermediate compounds of congruous or incongruous fusion Ln_nO_{2n-2} ($n=4,7,10,11,12,\propto$): the two ends of the series Ln_2O_3($n=4$) and LnO_2($n=\propto$) respectively present C-type and fluorite structures. In both, the Ln coordination is six but in the former it is not exactly an octahedron, but involves a distorted fluorite structure with the disappearance of tetrahedral oxygen for every four. The other intermediate oxides present variable coordination numbers: thus, the Pr_7O_{12}($n=7$) crystals can be visualised as rows of LnO_6 groups, which generate parallel sheath-like LnO_7 groups. The resulting rods are parallel to each other in the direction <111>.

On heating the LnO_7 phase, oxygen outgassing takes place on establishing non-stoichiometric equilibrium Ln_nO_{2n-2} ($n=4,7,10,11,12,\propto$): this outgassing depends on the firing temperature as well as on the glaze dissolution capacity and the microstructure of the colouring particle. The permanency of the defect in the glazes depends on glaze sealing temperature.

2. OBJECTIVES

This study analyses the outgassing phenomenon of a Pr-CeO_2 colourant obtained with different microstructures (ceramic colourant produced by calcination at 1400°C and coprecipitated colourant produced at 1150°C) in three typical types of ceramic tile matrices (twice-fire glaze, porous single-fire glaze and porcelain tile body). The results allow establishing the reaction mechanism and parameters that control outgassing, enabling appropriate matrix colouring.

3. EXPERIMENTAL

Samples were prepared of composition $0.05Pr_2O_3.CeO_2$, mineralised with 10 % fluorides, following two synthesis routes: (a) ceramic sample RC produced by mixing in a ball mill in acetone medium of Pr_6O_{11} and CeO_2 supplied by J.J. Navarrro S.A. The dry powder was calcined at 1400°C/2h, (b) coprecipitated gel sample RG obtained from cerium chloride (III) and Pr_6O_{11} supplied by Panreac for analysis, dissolved in excess concentrated HCl, gelling the solution with concentrated ammonia and drying it. The dry powder was mixed with the mineraliser and calcined at 1150°C/2h.

Figure 1 presents the microstructures produced with both methods. It shows the aggregated microstructure with large particles in the ceramic sample, with a smaller disaggregated particulate in the precipitated sample. The powders were glazed at 2% in three matrices: (a) twice-fire glaze fired in a twice-fire cycle of 110 minutes and 1000°C peak temperature, (b) monoporosa frit with a monoporosa of cycle of 60 minutes at 1080°C and (c) a porcelain tile matrix fired for 55 minutes at 1180°C. In general, as Fig. 2 shows, trapped gas is found in the case of the twice-fire matrix without causing any surface defects, the porous single-fire matrix presents profuse gaseous occlusion, making the material unusable, while no important defects occur in the porcelain tile. The L*a*b * colours are as follows: for RC: 44/5/19/15 (twice-fire), 90/15/8 (monoporosa), 96/2/-2(porcelain tile) and RG: 62/21/25 (twice-fire), 84/17/15 (monoporosa), 87/18/13 (porcelain tile), i.e., the ceramic sample tends to develop more intense, brownish colours, and the coprecipitated sample orange reds; the gel sample also colours the porcelain tile but the ceramic sample fails to do so. On the other hand, micronising the samples increases the outgassing defect (Fig. 2. b and c).

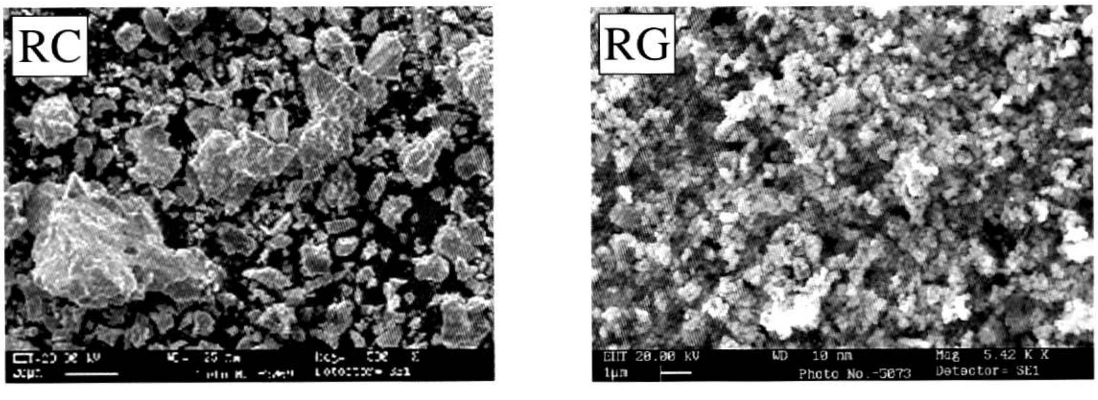

Figure 1: Microstructure of calcined samples RC and RG.

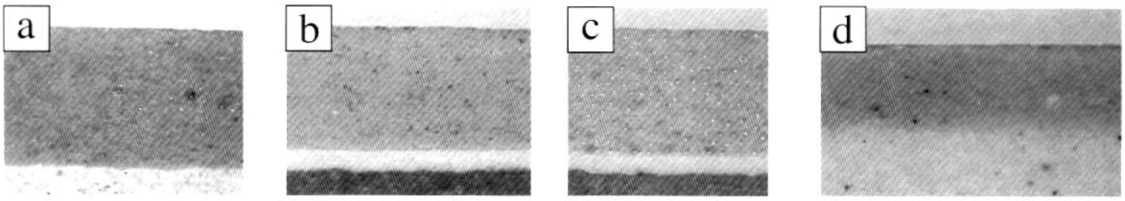

Fig. 2. Cross sections of different glazings: (a) RG twice-fire, (b) RC monoporosa, (c) RC micronised monoporosa, (c) RG porcelain tile.

CeO_2 decomposes according to the reaction $2CeO_2 \rightarrow Ce_2O_3 + 1/2O_2$, which is the basis for the use of cerianite as a three-way catalytic substrate in automobiles, cleaning HC, CO and NO_x emissions. The extent of this reaction determines the oxygen storage capacity (OSC) of the catalytic converter and depends on the crystalline structure and specific surface area of the material. The decomposition of cerianite takes place between 600 and 1100°C in a proportion, in the prepared samples, of around 0.3% for RG and of a little more than 0.1% for RC, measuring weight loss by thermogravimetric analysis.

The decomposition temperature range makes it clear that the twice-fire glaze which matures at 750-800°C allows outgassing without problems, the porcelain tile body which matures at 1160-1240°C still has quite a porous structure in the outgassing phase and has no problems either. However, the monoporosa glaze which matures at 1050-1120°C and seals at 960-980°C traps the gas, with high melt viscosity hindering efficient outgassing. As a result, the pigment is not suitable for these matrices. On the other hand, the effect of specific surface area on the oxygen storage capacity can be observed: the material RG with the largest specific surface area associated with its smaller particle size exhibits greater oxygen losses in TG than ceramic sample RC, while micronising the samples raises the outgassing problem.

4. CONCLUSIONS

Red praseodymium-cerianite pigments produce interesting colourings for ceramic twice-fire matrices and porcelain tile body colouring. However the decomposition process $2CeO_2 \rightarrow Ce_2O_3 + 1/2O_2$ make these pigments unsuitable for monoporosa glazes. This problem is further aggravated if the pigments are micronised, when the decomposition activated.

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