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Diffusion of Cr–Fe–Al–Zn pigment in a zirconia glaze[☆]

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Abstract

Commercial samples of a white zirconium frit and a Cr–Fe–Al–Zn pigment were used as a diffusion pair. Interdiffusion was observed at temperatures >1000 °C, indicating that the growth of the formed interface can be described by a parabolic function, which is dependent on the diffusion coefficients of the reacting elements, the chemical potential of these elements and the system geometry.
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1. Introduction

Glazing and serigraphic decoration are the final processes in the ceramic tile industry: they are responsible for the technical and aesthetic characteristics of the products [1,2]. Therefore, the importance of the study of ceramic diffusion mechanisms and kinetics is evident, particularly between pigments or pigments and frits. Diffusion studies in ceramic materials are generally related to binary or, at most, ternary systems [3]. However, ceramic glazes, tiles and many pigments are constituted by hydrated aluminosilicates based on alkaline and earth alkaline elements. The most common oxides in ceramic materials are SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O, TiO_2 and Fe_2O_3. Thus, the use of existing simple diffusion models for pairs of ceramic oxides is reasonable, since these models can provide important information, both quantitative and qualitative, relative to the mechanism and, at posterior stages, to the kinetic of diffusion in ceramic materials.

Divalent cations are diffused much more slowly at a given temperature than those which are monovalent; their activation energies are generally much larger. Nevertheless, this appears not to be directly related to the transport of modifier cations and material flow properties. For example, the activation energies for viscous flow in compositions of $SiO_2 \cdot CaO \cdot NaO$ systems present typical values of 100 kcal/g; the activation energy for Na ion diffusion is much lower, close to 25 kcal/g [3]. Such differences are not unexpected, because the processes in viscous flows and in diffusion are significantly different. The data for viscous flow can be better correlated with the diffusion of former cations in a glass structure (Si, in this case). The diffusion coefficients of modifier cations are generally larger in quenched glass than in well annealed glass with the same composition.

This difference can be significant in some cases, leading to differences in the specific volumes of glass, and glass with a greater volume and more open structure is characterized by greater diffusivity. Many monovalent cations can be substituted by Na ions, even at temperatures below the glass transition region. Li and K ions can be partially substituted by Na ions under similar conditions; however, if the exchange is exaggerated, tensions can appear in the glass structure with a sufficient intensity to promote its fracture. The substitution of one ion for another one (ionic exchange) is widely used as a technique to increase mechanical resistance in glass.

Interdiffusion [3–6] between two ceramics can be considered as the formation of a reaction product; this reaction product is better described as a solid solution instead of

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a distinct or separate phase. The formed solid solution is almost ideal; such that, the chemical potential is directly related to the composition (concentration) by $\mu_i = \mu_i^0 + \mathrm{R}T \ln \gamma c_i$, where the activity coefficient γ is equal to one [7]. Thus

$$\tilde{D} = \left[D_1^T X_2 + D_2^T X_1\right]\left(1 + \frac{\mathrm{d}\ln \gamma_1}{\mathrm{d}\ln X_1}\right) = D_1^T X_1 + D_2^T (1 - X_1) \tag{1}$$

is the Darken equation, assuming local equilibrium in any part of the interdiffusion region [8].

When the reaction product formation rate is controlled by diffusion through a planar layer across the product, a parabolic rate law [8] can be observed, in which the diffusion coefficient for processes is limited by rate. The planar layer thickness of the reaction product is given by the parabolic relation y as:

$$y = \left(2K\rho\kappa\frac{2\gamma}{r}\right)^{1/2} t^{1/2} \tag{2}$$

where K is the permeation coefficient (dependent on the particle size, packing factor, viscosity and temperature), ρ is the density of the product layer, κ is a factor that converts the volume removed to the volume deposited, $2\gamma/r$ is the capillarity pressure and t the reaction time. This parabolic rate law is very common for kinetic processes, where the limitation stage is the mass transport through the reaction layer.

In most ceramic technology processes the reactions in solid state occur by an intimate powder mixture [4,5,9]. This modifies the particle geometry and the reactions that occur on their surfaces. If the reaction occurs isothermally, the formation rate of the reaction zone depends on the diffusion rate [10]. For the initial stages of the reaction, the growth rate of the interfacial layer is given by the parabolic relation y.

For spherical geometry, the parabolic relation y can be written as $y = r(1 - \sqrt[3]{1-\alpha})$, where α is the reacted material volume and r the spherical radius [11]. This relation encompasses many solid state reactions, including silicate systems, ferrite formation, reactions to form titanates and other ceramic processes of interest. The equation is valid only for small thicknesses of reaction Δy and does not consider the change in molar volume between the reagents and the product layer [10].

The calculation of the reaction rates given by such relations on an absolute basis requires knowledge of the diffusion coefficient for all ionic species and knowledge of system geometry and the chemical potential for each species with regard to its position in the reaction product layer. The species that diffuse and control the reaction rate are the fastest moving ions, or ions and electrons capable of arriving at the boundary phase interface [11]. All the limitations discussed must be considered.

Another difficulty in detailed quantitative calculations is the strong dependence of the reaction rates on the structure of the reaction product [11–13]. In many cases the structure (lattice parameters) of the reaction product is formed in such a way that it is not coherent with the structure of the reagents, that is, the crystal habit of the products is different from the crystal habit of the reagents. Due to volumetric alterations its formation can occur with many defects and fissures. Consequently, there is a good chance of superficial and contour diffusion and the diffusion coefficient indicated in the relations is not necessarily identical to the diffusion in a monocrystal or a dense polycrystalline body; these values indicate an inferior limit for the actual diffusion coefficient and the possible rate of reaction [14–22].

The study of diffusion processes in glaze coatings for ceramic tiles is a major step in the control of the firing stage. Tonality and color variation are strongly influenced by the firing conditions. So, this work aims to study the influence of the firing temperature in the layer thickness of a brown pigment over a white zirconia glaze used to cover ceramic tiles.

2. Materials and methods

For this study, a frit and a pigment were used as raw materials, both from industrial sources (Table 1).

The white zirconium frit powder (passed through a 45 µm sieve) was compacted in a laboratory press at 25 MPa with addition of 2 wt% of water as a binder, resulting in sample cylinders of 10 mm in diameter by 10 mm in height. Thus, the compact bodies were dried at 110 °C for 2 h and then

Table 1
Physical–chemical characteristics of the raw materials

White zirconium frit (manufacturer's data)

Chemical composition (w%)

SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	B_2O_3	ZnO	ZrO_2
52.7	6.6	8.4	3.7	0.4	3.9	4.0	11.0	9.3

Critical temperatures (°C)

Glass transition (T_g)	Softening point (T_w)	Melting point (T_m)
535	790	1180

Pigment (manufacturer's data)

Color	Maximum use temperature (°C)	Density (g/cm^3)
Caramel brown	1300	4.8

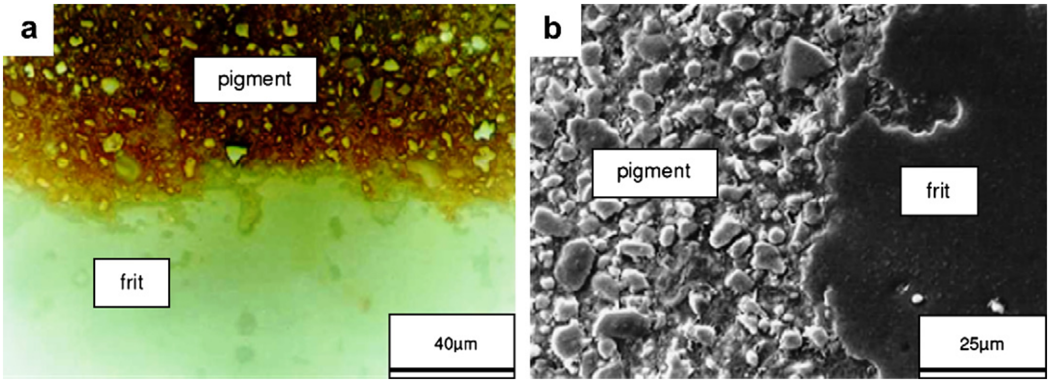

Fig. 1. Sample micrographs of a frit–pigment pair sintered at 900 °C for 1 h 30 min: (a) OM; (b) SEM.

presintered at 1000 °C for 15 min. The objective of this step was to obtain a body with adequate resistance to handling, because after several attempts to compact the frit–pigment pair at the same time, observation revealed that the compact bodies did not present sufficient mechanical resistance.

So, the pigment was mixed with water, forming a dispersion, and this dispersion was applied to the presintered frit compacts. The compacts were dried again, forming the frit–pigment pair for final sintering. The samples were sintered in a laboratory thermogradient oven under the same thermal cycle, with a heating rate of 5 °C/min at three different temperatures: 900 °C, 1000 °C and 1020 °C. The sintering time at the maximum temperature was 1 h 30 min and the samples were cooled in air; the samples were previously cooled in the oven. Finally, the sintered samples were wrapped in aluminum sheets, inlaid in bakelite, sectioned and properly polished. The microstructural analysis was carried out by optical (OM) and scanning electron microscopy (SEM). Three samples were analyzed (measured) at each treatment temperature to determine the average layer thickness.

3. Results and discussion

The diffusion process that occurs in silicate systems is the interdiffusion between solids. It was possible to verify the existence of interdiffusion in the frit–pigment system (Figs. 1–4) caused by the pigment dissolution in the frit glass matrix. The layer of interdiffusion formed during the sintering process was determined using SEM (average of five measurements). Observation revealed that at 900 °C, the formation of a diffusion interface (Fig. 1a) does not occur, showing that despite good sintering of the samples, demonstrated by the spherical form of the pores, the energy applied to the system (temperature) was not sufficient to promote diffusion at the visible scale under an optical microscope. In the scanning electron microscope (Fig. 1b) observation clearly revealed that no interdiffusion occurred at 900 °C.

The reaction product was initially observed at 1000 °C: it is the clearer region between the pigment (dark color) and the frit (white) (Fig. 2a). If the diffusion coefficients and the chemical potentials of both frit and pigment were available, it would be possible to estimate the thickness of the reaction layer formed with good accuracy. The reaction interface lightly contrasts (Fig. 2b) with the reagents (frit and pigment). The perfectly spherical form of the frit pores is clear, indicating their complete glass phase formation. The apparent thickness of the layer is approximately 20 μm.

Finally, at 1020 °C the interdiffusion layer formation is clearly verified, with an average apparent layer thickness of 100 μm (Fig. 3).

A line profile analysis (energy dispersive spectrometry, EDS microprobe) was carried out for the three samples to identify the presence of the element Cr (Fig. 4). At 900 °C (Fig. 4a), observation showed discontinuity in the Cr line

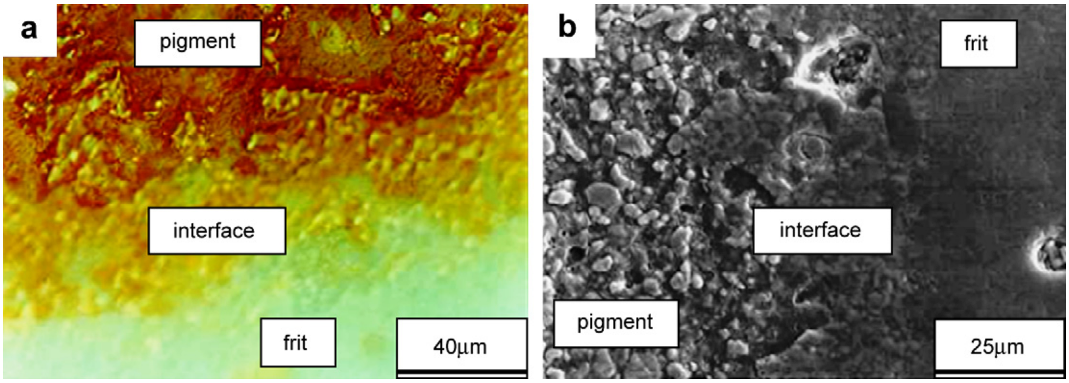

Fig. 2. Sample micrographs of a frit–pigment pair sintered at 1000 °C for 1 h 30 min: (a) OM; (b) SEM.

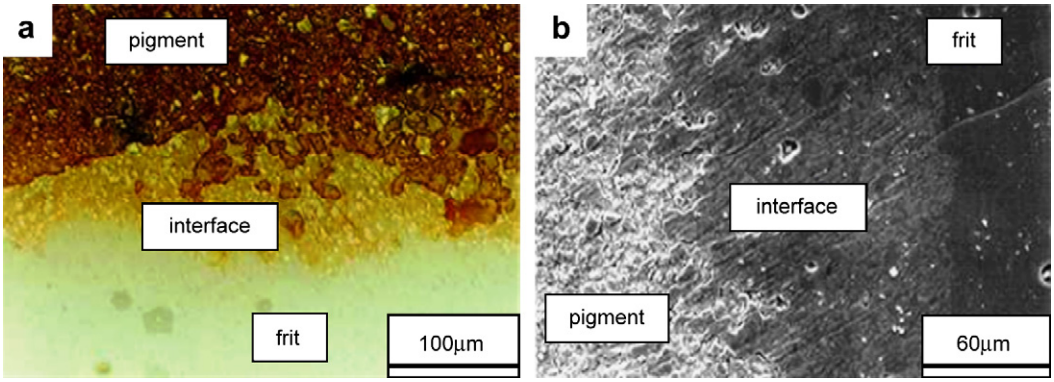

Fig. 3. Sample micrographs of a frit–pigment pair sintered at 1020 °C for 1 h 30 min: (a) OM; (b) SEM.

profile, initiating at the pigment and continuing into the frit, indicating that an interface was not formed. At 1000 °C (Fig. 4b), a transition between frit and pigment is visible at the same position, indicating the presence of an interface that contains Cr. In fact, at 1020 °C (Fig. 4c), an interdiffusion layer was formed and confirmed by the line profile analysis for Cr element. A line profile analysis for the element chromium was used, because it is not present in the frit and is easily measured by EDS microprobe.

Finally, Fig. 5 shows the diffusion thickness as a function of the temperature treatment of the studied system. The layer thickness shows a parabolic relation with the treatment temperature.

4. Conclusion

The results from the optical (OM) and scanning electron microscopy (SEM) and from energy dispersive spectrometry (EDS microprobe) and line profile analyses, verified the occurrence of the interdiffusion process between solids for the pair zirconium frit and pigment of the Cr–Fe–Al–Zn system at temperatures above 1000 °C. The mathematical model for layer thickness determination of the formed interface is a parabolic function dependent on the diffusion coefficients of the reacting elements, the chemical potential of these elements and the system geometry.

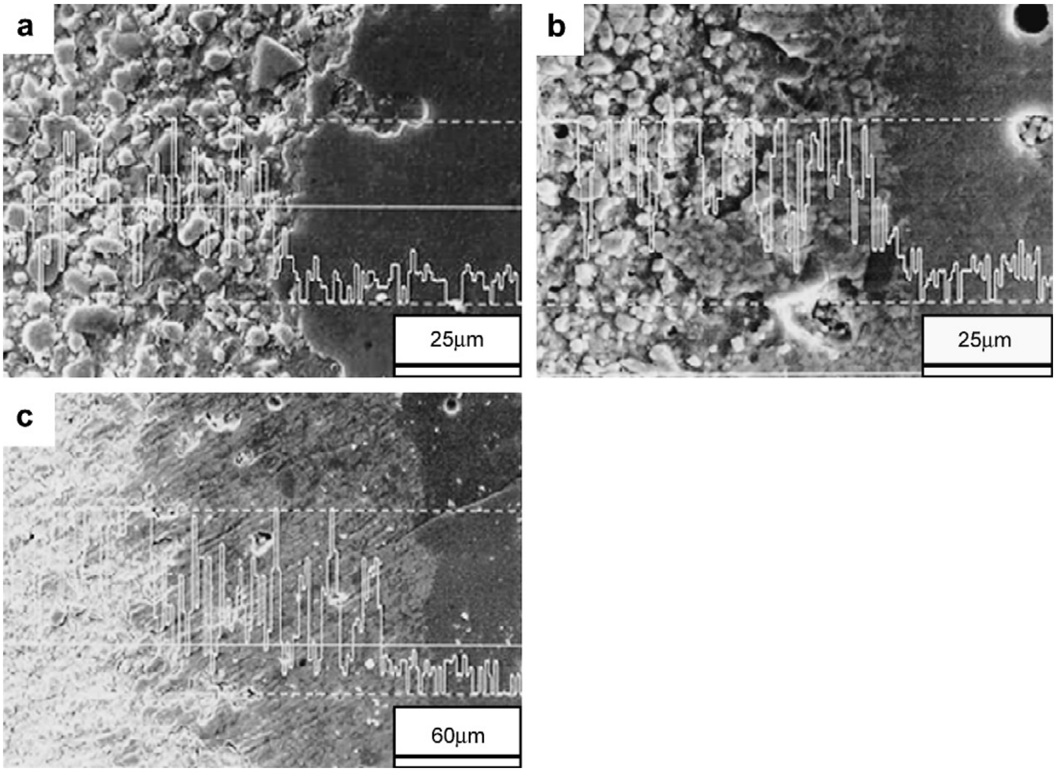

Fig. 4. Sample micrographs (SEM with EDS microprobe line profile analysis) of frit–pigment pairs sintered at (a) 900 °C, (b) 1000 °C and (c) 1020 °C for 1 h 30 min.

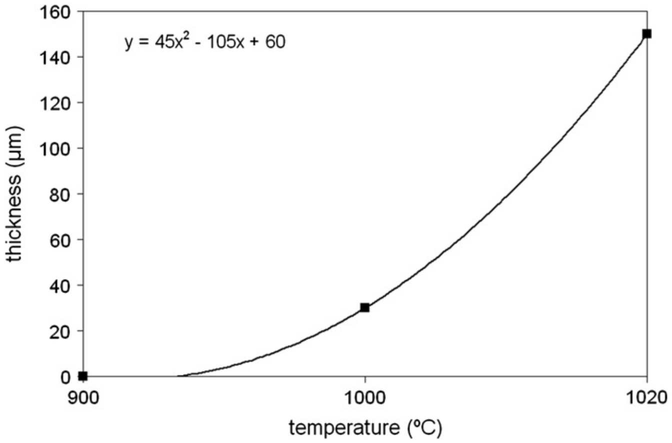

Fig. 5. Parabolic relation between the pigment layer thickness and the sintering temperature.

The layer interface thickness was only determined experimentally, due the lack of information regarding diffusion coefficients and other parameters, but the values of thickness show a parabolic relation with the treatment temperature. In spite of this the experiment is reproducible: if all other industrial conditions are the same (mainly glaze permeability and kiln atmosphere) the layer thickness will only be determined by the treatment temperature as a parabolic function.

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