

DIFFUSION IN CERAMIC MATERIALS: A PRELIMINARY STUDY

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ABSTRACT

The present work deals with the preliminary results of a study on diffusion in ceramic materials. A white zirconium frit and a pigment pertaining to the Cr-Fe-Al-Zn system were used as a diffusion pair, both of industrial origin. The occurrence of an interdiffusion process was observed in temperatures above 1000°C, indicating that the growth of the arising 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 system geometry.

Key words: Ceramic diffusion; SEM; EDS; zirconium frit; Cr-Fe-Al-Zn pigment.

1. INTRODUCTION

In the single-firing ceramic tile industry, glazing and screen printing processes are very important for attaining products with good technical and aesthetic characteristics^{[1],[2]}. This therefore evidences the importance of the study of ceramic diffusion mechanisms and kinetics, particularly between pigments or pigments and frits. Diffusion studies in ceramic materials generally relate to binary systems and, at most, to ternary ones^[3]. However, ceramic glazes, tiles and many pigments contain hydrated aluminosilicates based on alkaline and alkaline earth elements. The most common oxides in ceramic materials are SiO₂, Al₂O₃, CaO, MgO, K₂O, Na₂O, TiO₂ and Fe₂O₃. It is therefore reasonable to use existing simple diffusion models for pairs of ceramic oxides; these models thus can provide important quantitative and qualitative information relating to the mechanism and, in a subsequent stage, to the diffusion kinetics in ceramic materials.

Divalent cations diffuse much more slowly than monovalent ones at a given temperature; their activation energies are generally much larger. Nevertheless, there does not seem to be a direct relation between the transport of modifier cations and materials flow properties. For example, the activation energies for viscous flow in compositions of SiO₂.CaO.NaO systems present typical values of 100kcal/g.at; the activation energy for Na ion diffusion is much lower, close to 25kcal/g.at^[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 correlated better with the diffusion of former cations in a glass structure (Si, in this case). The diffusion coefficients of modifier cations in glasses that are rapidly cooled in the glass transition region are generally larger than those in well-annealed glasses with the same composition.

In some cases this difference can be significant, leading to differences in the specific volumes of glasses, and glasses with larger volume and opened structure are characterized by a 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, stresses can appear in the glass structure with sufficient intensity to produce fracture. The substitution of one ion by another one (ionic exchange) is widely used as technique to increase mechanical resistance in glasses.

Interdiffusion^{[3],[4],[5]} 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 a distinct or separate phase. The solid solution formed is almost ideal; in this way, the chemical potential is related directly to the composition (concentration) by $\mu_i = \mu_i^0 + RT \ln \gamma_i$, where the activity coefficient γ is equal to one. Thus

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

the Darken equation, assuming local equilibrium in any part of the interdiffusion region.

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

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

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

In most ceramic technology processes, solid state reactions occur by an intimate powder mixture^{[4], [5]}. This modifies the particle geometry, and the reactions occur at their surfaces. If the reaction occurs isothermally, the formation rate of the reaction zone depends on the diffusion rate. For the initial stages of the reaction, the growth rate of the interface layer is given with a good approximation by the parabolic relation y .

For a 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. This relation includes many solid state reactions, including the silicate systems, ferrite formation, reactions to form titanates and other processes of ceramic interest. The equation is valid only for small reaction thicknesses Δy , and it does not consider the change in molar volume^{[4], [5]} between the reagents and the product layer.

The calculation of the reaction rates given by such relations on an absolute basis requires knowing the diffusion coefficient for all the ionic species and knowing 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 those ions that move quicker, or the ions and electrons capable of reaching the boundary phase interface. 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. In many cases, the reaction product is formed in such way that it is not coherent with the reagents. Due to volumetric alterations, it can form with many defects and fissures. Consequently, there is a good chance for surface and contour diffusion, and the diffusion coefficient indicated in the relations is not necessarily identical to the diffusion in a monocrystal or in a dense polycrystalline body; these values indicate a lower limit for the actual diffusion coefficient and the possible rate of reaction.

When new phases are formed, such as by carbonate decomposition at low temperatures, there is a strong tendency for the initial network (structure) parameters to have a non-equilibrium value, corresponding to a structure and interface not coherent with the reagent, due to nucleation and growth effects.

The diffusion coefficients for this network in a non-equilibrium state are normally larger than those for the final product in equilibrium. For example, an increase in the solid state reaction rate at polymorphic transition temperature (Hedvall effect) is frequently observed^[3]. This effect is related to network deformations and fissures formed by volume alterations at the transition point; these network deformations and fissures occur extensively in quartz, for example, in which the volume change is great. There is also a tendency for equilibrium to occur between two polymorphic forms at transition temperature, with a coherent interface raising the deformations of the network, increasing the diffusion coefficients and the opportunity of mass transfer.

2. MATERIALS AND METHODS

white zirconia frit (manufacturer's data)								
chemical composition [wt%]								
SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	B ₂ O 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								
colour			maximum temperature used [°C]			density [g/cm ³]		
caramel brown			1300			4.8		

Table 1. Physico-chemical characteristics of the raw material.

For this study we used a frit and a pigment as raw materials, both of which were industrial. Some technical specifications are listed in table 1.

The white zirconia frit powder (325 mesh) was compacted in a laboratory press at 25MPa with the addition of 2 wt% water as a binder, resulting in sample cylinders of 10mm in diameter and 10mm height. Thus, the compact bodies were dried at 110°C for 2h and then pre-sintered at 1000°C for 15min. The objective of this step was to obtain a body with adequate resistance to handling, because after some attempts to compact the frit-pigment pair, it was observed at the same time that the compacted bodies did not have mechanical resistance.

The pigment was thus mixed with water, forming a dispersion, and this dispersion was applied onto the pre-sintered 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 1h30min and the sample cooling was in air (the samples had been cooled in the oven). Finally, the sintered samples were wrapped in aluminium sheets, inlaid in bakelite, sectioned and

properly polished. Microstructural analysis was carried out by optical and electron microscopy (OM and SEM).

3. RESULTS AND DISCUSSION

The diffusion process that occurs in silicate systems is interdiffusion between solids. Although it was not possible to determine quantitatively the layer of interdiffusion generated during the frit-pigment sintering process, in addition to the fact that this goes beyond the initial objective of this work, it was possible to perceive the existence of interdiffusion in some micrographs. It was observed that at 900°C, there was apparently no formation of a diffusion interface (figure 1a), showing that despite the good sintering of the samples, evidenced by the spherical form of the pores, the energy applied to the system (temperature) was not enough

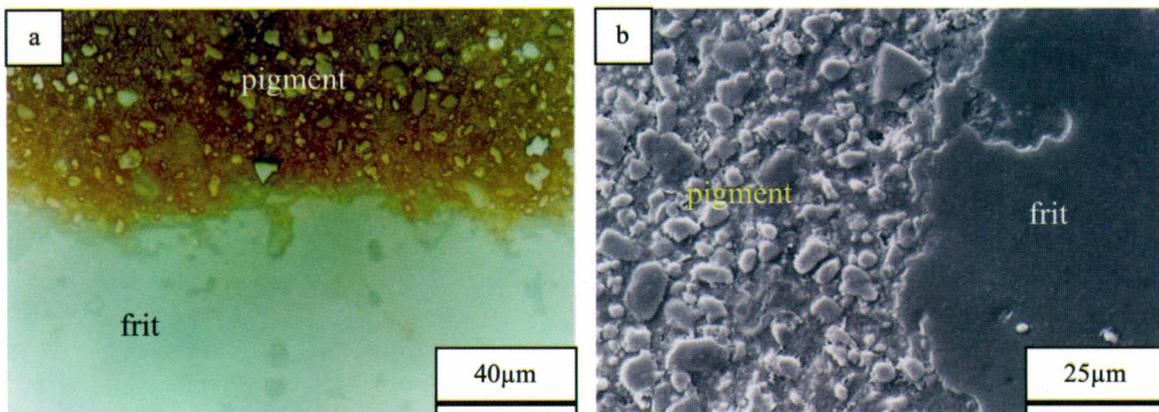


Figure 1. Sample micrographs of the frit-pigment pair sintered at 900°C for 1h30min: (a) OM; (b) SEM.

to promote diffusion on a visible scale in the optical microscope. In the scanning electron microscope (figure 1b) it was observed that at 900°C there was really no interdiffusion.

Beginning at 1000°C, the formation can be observed of a reaction product, indicated (figure 2a) by the clearest region between the pigment (brown colour) and the frit (white). If the diffusion coefficients and the chemical potentials of frit and pigment were available, it would be possible to calculate with a good accuracy the thickness of the reaction layer that forms. The reaction interface contrasts lightly (figure 2b) with the reagents (frit and pigment). The perfectly spherical form

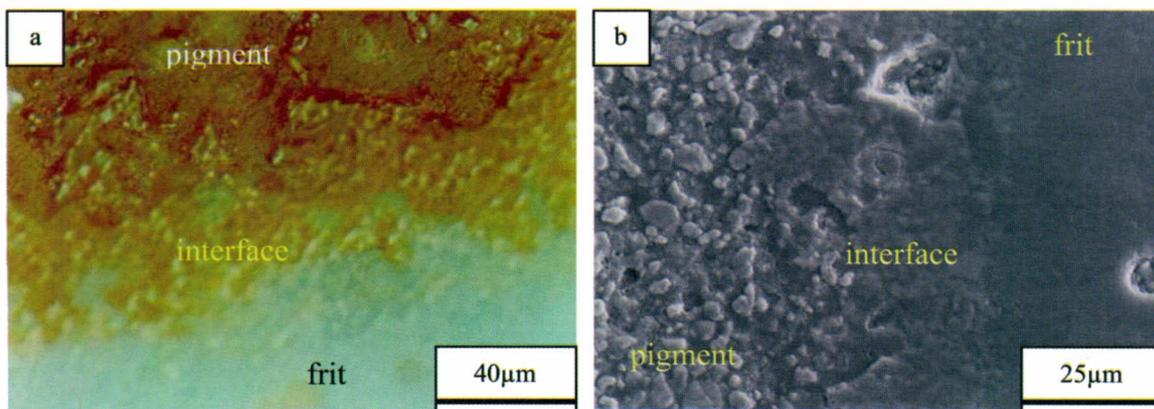


Figure 2. Sample micrographs of frit-pigment pair sintered at 1000°C for 1h30min: (a) OM; (b) SEM.

of the frit pores is clear, indicating its complete glass phase formation. The apparent thickness of the layer is approximately $20\mu\text{m}$.

Finally, at 1020°C the interdiffusion layer formation is clearly perceived, with an average apparent layer thickness of $100\mu\text{m}$ (figure 3).

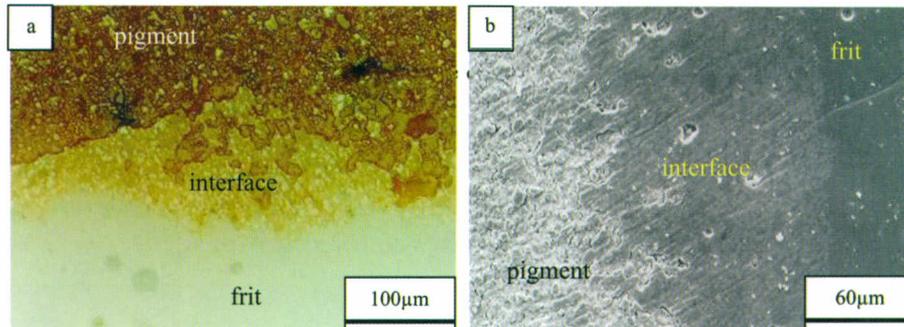


Figure 3. Sample micrographs of the frit-pigment pair sintered at 1020°C for 1h30min: (a) OM; (b) SEM.

A line profile analysis (EDS microprobe) was carried out for the three samples to identify the presence of Cr element (figure 4). At 900°C (figure 4a) a discontinuity can be observed in the Cr line profile beginning at the brown pigment into the white frit, indicating that an interface has not formed. At 1000°C (figure 4b) it is perceived, for the same position, a transition between frit and pigment, indicating the presence of an interface that contains Cr. In fact, at 1020°C (figure 4c) an interdiffusion layer has formed, confirmed by the line profile analysis for the Cr element. The line profile analysis for the chromium element was used because it is not present in the frit and it is easily measured by the EDS microprobe.

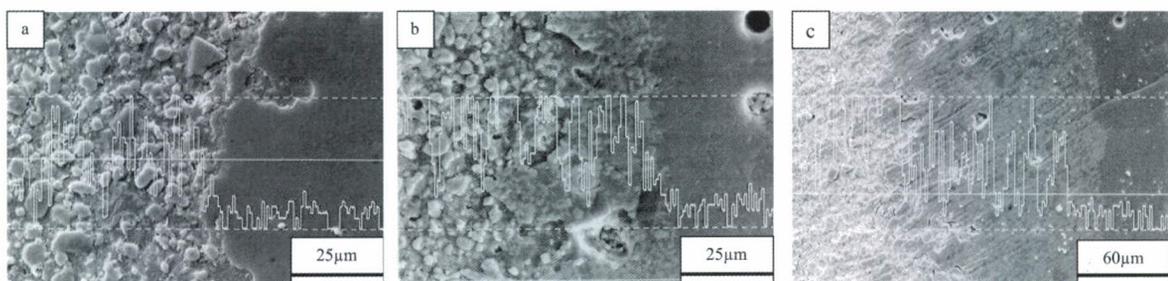


Figure 4. Sample micrographs (SEM with EDS microprobe line profile analysis) of frit-pigment pairs sintered at (a) 900°C , (b) 1000°C and (c) 1020°C for 1h30min.

4. CONCLUSION

Optical (OM) and scanning electron microscopy (SEM) results and EDS microprobe and line profile analyses showed the occurrence of an interdiffusion process between solids for the pair zirconia frit and Cr-Fe-Al-Zn system pigment at temperatures above 1000°C . The mathematical model for determining the layer thickness of the interface that forms is a parabolic function dependent on the reacting element diffusion coefficients, chemical potential of these elements and system geometry.

The layer interface thickness was only determined experimentally, due the lack of information on the diffusion coefficients and other parameters.

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