Simultaneous measurement of coefficient of thermal expansion and biaxial modulus of enamel thick films deposited on glass substrates by curvature technique

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Abstract
The measurement of the thermoelastic properties of enamel thick films deposited onto soda-lime silicate glass is challenging. The film properties can be modified by the interdiffusion between the glass substrate and the enamel and by the crystallization that occur during the sintering. The average biaxial modulus and coefficient of thermal expansion of several enamel thick films deposited onto 700 µm glass substrates have been simultaneously measured using the curvature method. The value of the coefficient of thermal expansion measured with a dilatometer on enamel bulk samples is significantly higher, associated with the absence of diffusion and a different enamel structure. The interdiffusion of elements between the enamel film and the glass substrate has been demonstrated with Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The amount of porosity ratio presents in the enamel film, evaluated via Scanning electron microscopy(SEM), has a great influence on the biaxial modulus. The amount of compressive stress in the enamel, calculated from the film thermoelastic properties, is strongly correlated with the mechanical performance of enameled glasses, investigated by Ring On Ring methods. Therefore, a high Young’s modulus for the enamel and a mismatch of the coefficient of thermal expansion between the enamel film and substrate, the film having the lowest value, has been found to increase significantly the mechanical performance of the stack.

KEYWORDS
biaxial modulus, coefficient of thermal expansion, curvature measurement, enamel, thick-film

1 | INTRODUCTION

Enamel thick films deposited onto soda-lime silicate glass are widely employed in many applications, such as automotive and architectural glass. In many cases the enamel is first deposited on the flat glass that is later deformed by gravity or mechanical load after heating above the glass softening temperature. The glass enamel, composed of a low-melting glass frit containing an oxide pigment, is required for UV protection and decorative purposes. However, enamel thick
films have a significant weakening effect on the mechanical strength of the enameled glass. The degradation of the glass strength after enameling has been studied previously, revealing through fractographic analysis of broken samples that the failure is initiated from porosities and pigment aggregates in the enamel film. Then this failure propagates to the glass substrate.\(^1\)\(^-\)\(^3\) Additionally, the mechanical properties of enamel thick films, such as the apparent indentation fracture toughness, Young’s modulus and hardness, have been investigated by nanoindentation.\(^1\) Until now, the effect of the residual stresses present in the enamel film on the robustness of the complete stack has not been investigated. The determination of the residual stress state in enamel thick films, the weakest material where the failure initiates, is essential to provide a deeper comprehension on the in-service failure mechanisms. Indeed, the beneficial effect of surface compressive stresses for glass systems, generated by thermal tempering, is well documented.\(^4\)\(^-\)\(^8\) Therefore, the thermoelastic properties of films can differ from the value measured on a bulk material having the same initial chemistry. The thermal treatment, required to fuse the enamel, required for the prediction of the development of residual stress in the thick film upon cooling, are presented in this paper. The scope of this paper is the simultaneous characterization of the biaxial modulus and coefficient of thermal expansion of enamel thick films deposited on glass substrates by curvature technique. The curvature technique is generally employed for the characterization of thin films.\(^9\)\(^-\)\(^11\)

In this work, the technique is employed to characterize the properties of enamel thick films by adjusting the substrate thickness. The advantage of this inexpensive technique over standard method such as dilatometer or thermomechanical analysis (TMA) resides in the quantitative determination of the thick film thermoelastic properties as deposited onto the glass substrate, rather than analyzing bulk enamel samples. Indeed, the thermoelastic properties of films can differ from the value measured on a bulk material having the same initial chemistry. The thermal treatment, required to fuse the enamel, induces defects in term of porosities. The porosities ratio reduces significantly the average Young modulus of the enamel film.\(^12\)\(^,\)\(^13\) Additionally, the interdiffusion of elements, such as alkalis, between the glass substrate and the film during the thermal treatment modifies locally the film composition, and therefore, the average coefficient of thermal expansion (CTE) of the film. Furthermore, the enamel is partially crystallized during the thermal treatment, comprising bismuth and zinc silicates, and copper chromite spinels.\(^14\) The crystallinity ratio between the film and bulk material might differ, because the samples have different thickness, hence, different heating and quenching rate.

The objective of this paper was to characterize the role of the residual stresses in the enamels on the mechanical strength of the enameled glasses and to elucidate the mechanism for the formation of these stresses. The amount of compressive residual stress in the enamel can be calculated from the film thermoelastic properties. Therefore, the biaxial modulus and coefficient of thermal expansion of three different glass enamel thick films deposited onto different 700 µm glass substrates have been simultaneously measured using the curvature method. The value of the coefficient of thermal expansion has been compared with the value measured with a dilatometer on enamel bulk sample. Deeper insights on the mechanisms for the construction of residual stresses in the enamel have been obtained from the investigation via Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and Scanning electron microscopy (SEM). Finally, the mechanical properties of the three different enamel suppliers have been characterized by Ring-On-Ring (ROR) onto 3.85 mm thick enameled glasses, corresponding to the typical automotive glasses thickness. The correlation between the mechanical performance, the residual stress and the thermoelastic properties provides a deeper understanding in the actual in-service failure mechanisms of the enameled glasses.

2 \ | \ THEORETICAL BACKGROUND

2.1 \ | \ Evolution of film stresses by curvature measurement

The thermal expansion coefficient and biaxial modulus of thick films can be determined by measuring the evolution of stresses in the thick film during a heating cycle using a curvature measurement set-up (Figure 1).\(^9\)\(^,\)\(^10\)\(^,\)\(^15\) The method is based on the measurement of the evolution of curvature of an anisotropic substrate recovered with the film, as a function of the temperature of the sample as placed inside an oven. The stresses ($\sigma_{film}$) in the film, induced by elastic property mismatch, introduce a macroscopic curvature to the substrate. The relation between the substrate curvature radius and the average stresses in the film is given by the Stoney formula\(^11\):

\[
\sigma_{film} = \frac{1}{6} \left( \frac{E}{1-\nu} \right)_{sub} \frac{t^2_{sub}}{t_f} \cdot \frac{1}{R}
\]

(1)

where $\sigma_{film}$ is the average residual stress in the coating, $E$ and $\nu$ are the Young’s modulus and Poisson’s ratio, $t$ the thickness, and $R$ the curvature radius. The subscripts f and sub refer to the film and the substrate. The residual stresses on the film are supposed to be biaxial axisymmetric, additionally, the substrate and the films are supposed to be linear elastic materials. The substrate curvature must be measured below the glass transition temperature in order to avoid stress relaxation due to the viscoelastic behavior of glass or the enamel. The Stoney formula can be used in the case where the film thickness is very small compared to the substrate thickness. Additionally, the maximum sample strain should remain smaller than the half of the substrate thickness to ensure a biaxial stress state in the system.\(^11\)
2.2 Measurement of the Coefficient of Thermal Expansion (CTE) and biaxial modulus of thin films

The change in curvature of different glasses coated by the film is measured as a function of the temperature. The macroscopic thermal stress in the film \( \sigma_{\text{film,th}} \) is calculated from the curvature using the Equation (1). This thermal stress change imposed to the film by the free dilatation of the substrate depend on the film’s elastic properties:

\[
\sigma_{\text{film,th}} = \left( \frac{E}{1 - v} \right)_{\text{film}} \cdot (\alpha_{\text{sub}} - \alpha_{\text{film}}) \cdot (T - T_0)
\]  

where \( \alpha \) is the thermal expansion coefficient. The subscripts “sub” and “f” refers to the substrate and to the film. \( T \) and \( T_0 \) are the temperature of the sample and the room temperature respectively. This equation can be used for relatively thick substrate compared to the layer thickness, ensuring that the substrate is infinitely more rigid than the film. The thermoelastic properties of thick films can be determined by depositing the enamel film on a set of substrates with different thermal expansion coefficient, in order to plot the \( \sigma_{\text{film}} \) in function of the temperature for each substrate. Finally, the slope \( \frac{\partial \sigma_{\text{film, th}}}{\partial T} \) should evolve linearly when plotted in function of the CTE for different glass substrates. As described by Equation (3), the slope of this regression line corresponds to the biaxial modulus of the film while the intercept with the x-axis corresponds to the thermal expansion coefficient of the film. Three to four different glass substrates are required to measure accurately the thermoelastic properties of the film.

2.3 Effective elastic moduli of Porous Materials

The porosity has a great influence on the effective Young’s modulus of a porous material. The effective Young’s modulus is usually expressed in terms of the Young’s modulus of the fully dense matrix and the porosity fraction present in the material. The model from Ramakrishnan and Arunachalam enables the prediction of the Young’s modulus \( (E) \) of a porous solid as a function of pore fraction \( (P) \) in case the Young’s modulus \( (E_0) \) and Poisson ratio \( (\nu_0) \) of the fully dense solid material is known:

\[
E = c \cdot E_0 (1 - P)^n
\]

where \( 0.1 \leq c \leq 4 \) and \( n \approx 2 \). The constant \( c \) is expressed by:

\[
c = \frac{1}{1 + (2 - 3 \cdot \nu_0) \cdot P}
\]
enamel is expected to have higher values compared to the values measured with the curvature measurement technique. However, the average residual stresses of the layers can be calculated with the average biaxial modulus of the complete layers.

### 2.4 Ring On Ring biaxial flexure testing

The mechanical properties of the different enamel suppliers have been characterized by Ring On Ring (ROR) onto 3.85 mm thick enamelled glasses, corresponding to the typical automotive glasses thickness.

The advantages of the Ring On Ring biaxial flexure testing method over uniaxial flexure tests, such as three-point bending test, resides in the higher repeatability of the breakage pattern due to the elimination of the edge effects. The maximum tensile stress generated in ROR test is calculated from the following equations:

\[
\sigma_{\text{Max}}^\text{ROR} = \frac{3P}{2\pi h^2} \left[ (1-\nu) \left( \frac{R_S^2 - R_L^2}{2R^2} \right) + (1+\nu) \ln \left( \frac{R_S}{R_L} \right) \right]
\]  

(6)

For a rectangular test specimen, \( b \) is the radius of a circle that expresses the characteristic size of the plate with edge length \( 2R' \) as follows:

\[
R = \frac{Rt \cdot \left(1 + \sqrt{2}\right)}{2} = 1.21 \quad Rt = 60.5 \text{ mm}
\]  

(7)

where \( P \) is the applied load, \( h \) the thickness, \( \nu \) the Poisson's ratio, \( D_S \) the diameter of the support ring, and \( D_L \) the diameter of the load ring, and \( l_1 \) and \( l_2 \) are the lengths of the sides of the plate.

The strength distribution for each experimental trial conditions is represented by a conventional two-parameter Weibull analysis as following:

\[
F = 1 - \exp \left[ - \left( \frac{\sigma}{\sigma_0} \right)^m \right]
\]  

(8)

where \( (F) \) is the failure probability, \( \sigma \) is the stress at failure, \( \sigma_0 \) is the Weibull characteristic strength, and \( m \) is the Weibull modulus describing the strength variability. The highest Weibull modulus \( m \) is, when the lower the breakage force is dispersed. The failure probability is calculated as follows:

\[
F = \frac{r - 0.5}{N}
\]  

(9)

where \( N \) is the number of specimens tested and \( r \) is the ranking of the strengths of the specimens. The weakest ranking is \( r = 1 \) being and the strongest ranking is \( r = N \). The term \( \sigma_0 \) is the scale parameter corresponding to the glass strengths where 63.2 percent of the samples have failed.

The Equation (8) can be written as:

\[
\ln [- \ln (1 - F)] = m \cdot \ln (\sigma) - m \cdot \ln (\sigma_0)
\]  

(10)

The Weibull modulus \( m \) is the slope of the linear regression and characteristic strength \( \sigma_0 \) is estimated from the Weibull plot.

### 3 EXPERIMENTAL PROCEDURE

#### 3.1 Enamed thin glasses

The curvature technique requires a set of thin isotropic commercial glass substrates with different thermal expansion coefficient. The Table 1 presents the thermoelastic properties and general composition of the different glasses substrates, provided by the suppliers, used in the experiment. The dimension of the glass samples is 70 × 70 × 0.7 mm³. The White float glass, AF45 and Eagle 2000 thin glass substrates have been supplied by the company Präzision Glas & Optik GmbH. The company Saint-Gobain has supplied the V95 and CS77 thin glass substrates. The initial thickness of the glass V95 was 1.5 mm, therefore, the substrates have been

| Glass name   | Composition         | CTE \( (10^{-7} \text{ K}^{-1}) \) (20-300°C) | E (GPa) | \( \nu \) |
|--------------|---------------------|------------------------------------------|---------|---------|
| Saint-Gobain V95 | Higher alkali content—SLS glass | 108 | 67     | 0.23    |
| White float glass | SLS glass           | 87 | 70     | 0.22    |
| Saint-Gobain CS77 | Lower alkali content—SLS glass | 77.5 | 76.4 | 0.238   |
| AF 45        | Alkali-free borosilicate | 45 | 66     | 0.235   |
| Eagle 2000   | Alkali earth borosilicate | 31.8 | 70.9 | 0.23    |

**TABLE 1** Thermo-elastic properties and composition of the thin glasses substrates required for the curvature technique
polished by the company OPA Opticad on the atmosphere side to reach a final thickness of approximately 700 µm. Three commercially available enamel pastes for automotive tempered glass were applied onto the glass substrate by screen printing technique, using a plain weave mesh. The three enamel pastes references are enamel n°1, enamel n°2, enamel n°3. The screen printing procedure of 700 µm thick glasses requires glass shims, with the same thickness as the glass substrate placed around the sample in order to avoid any displacement during the printing. Additionally, the glass is maintained onto the printing table by air suction system. The enamel is printed onto the tin side of the float glass substrates. The enamel is deposited with a 48 µm diameter thread with 90 threads per cm, resulting in a theoretical ink volume of 19 cm³/m². The composition of the enamel paste enamel n°2 has been analyzed, after thermal removal of the organics elements (solvent and resin) at 650°C, using X-Ray fluorescence and with ICP-OES. The enamel has a typical composition of 80 wt% bismuth zinc borosilicate glass frits and 20 wt% CuCr₂O₄ pigment particles. The film thickness has been measured with a MarSurf M 400 surface profilometer (Mahr GmbH). The screen printed glasses are dried at 160°C for 160 seconds in order to eliminate the solvents, reducing the amount of porosities after the sintering process. Then, the 700 µm thick glass samples are placed onto a 3.0-mm thick glass-ceramics to obtain similar thickness in order to reproduce the heat flow of a standard 3.8 mm glass. The stack, consisting of the sample and the glass-ceramic, is placed onto a metallic structure. Finally, the structure is inserted into the furnace. The complete stack undergoes a thermal treatment in a furnace at 745°C for 270 seconds in order to remove the remaining resin and fuse the enamel. The temperature of the glass sample reaches 650°C after the heating phase. The furnace temperature is adjusted in function of the fusibility of the different tested enamels, having in this case a firing range between 620°C and 650°C. After the sintering process, the samples are removed from the furnace, undergoing a slow cool down to room temperature. Finally, the thin glasses are cut into stripes for the curvature measurement, with a typical dimensions of 100 × 10 × 0.7 mm³. The thin glasses were cut using a cutting wheel with an angle of 105° to avoid damaging the glass.

3.2 | Curvature measurement set-up

A home-made apparatus curvature equipment has been used for the measurements (Figure 1). The curvature measurement test bench is composed of three main components placed in a close metallic structure, a Nabertherm oven (model LE 2/11/P300), a Samsung SyncMaster B1740R-LCD-TFT-17” screen and a monochrome digital camera (Figure 1). The samples and a flat reference are placed horizontally in the oven, for the heating cycle onto an alumina sample holder to ensure reproducibility of the curvature acquisition. The holder is composed of alumina rollers placed in a grooved plate. An open window made of fused-silica glass is present on the top of the oven to enable monitoring of the sample. The planarity reference is place in the oven beside the sample in order to correct the aberrations that could come from heating. The reference consists in a flat silica surface with thickness of 2.9 mm fabricated by the company OPA Opticad. The correction is made by subtracting the apparent curvature of the reference from the sample curvature. The screen is placed on top of the metallic structure, in alignment with the window to project white and black fringes on the sample and the reference. Finally, the digital camera provided by Basler, model piA2400-12 gm with 2448 × 2050 pixels and a sensor of 2/3”, is mounted besides the screen. The program HOLOMAP provided by the company HOLO3 allows full acquisition of the three-dimensional surface topography and curvature measurement of the sample. The evolution of the glass substrate curvature is determined by phase measuring deflectometry (PMD). A fringe pattern with sinusoidal profile is displayed vertically and horizontally onto a screen. The camera records the distorted image of the screen, which is reflected by the sample surface. The deformation of the initial light beam enables the reconstruction of the sample 3D shape using the FA4 (Fringe Analysis) software with the dll HoloMap. (Figure 1a). The curvature of the sample is measured each for 70 seconds. The maximum temperature in the oven is set to 400°C to induce the smallest amount of structural modifications to the film material. The heating rate is 25°C/min, the maximum temperature is kept for 5 min, after which the oven cools down according to its natural inertia. The evolution of the temperature in the oven during the experiment is recorded by the thermocouple next to the samples (Figure 1b). The slope δσ/δT is measured during the cooling down phase, as the complete sample is under thermal equilibrium due to slow cooling rate.

3.3 | Ring On Ring biaxial flexure testing

The mechanical properties of the different enameled regular white float glasses have been characterized by Ring On Ring (ROR) method following the European Standard EN 1288-1:2000. The sample dimension are 100 × 100 × 3.8 mm, the glass thickness corresponds to the typical thickness used for automotive glasses. Forty samples are produced for each experimental trial conditions to ensure a sufficient number of replicates and to assess accurately the experimental error. The screen printing and drying procedure is the same as explained previously for the thin glasses, the glass shim thickness had to be adapted to the specimen thickness. Then, the enameled glasses have
undergone a thermal treatment in a furnace at 700°C during 180 seconds in order to remove the remaining resin and to fuse the enamel. The temperature of the glass sample reaches 650°C after the heating phase. Finally, the stack undergoes a thermal tempering, by very fast blast cooling from 650°C to room temperature in 20 seconds, in order to increase the glass strength. The strength of the three series of enameled glasses have been studied with ring-on-ring (ROR) biaxial flexure testing methods on the tin side. The maximum stresses leading to the breakage can be calculated from the applied loads with Equation (6). The experimental setup is composed of two coaxial rings, the support ring with a diameter of 90 mm, and the loading ring with a diameter of 45 mm. The radius of curvature of each ring was 2.5 mm. The friction between the sample and support ring is reduced by employing 3mm-thick rubber sheets with a hardness of 40 ± 10 IRHD following the norm ISO 48. The glass surface is recovered with adhesive tape to retain fragments for fractographic analysis. The samples have been tested at a stressing rate of 2.0 MPa/s and the failure loads were recorded for each specimens in order to calculate their mechanical strengths.

### 3.4 Dilatometer sample

The thermoelastic properties of the enamel 2 thick film measured by curvature technique are compared to the CTE measured by the dilatometer on a bulk enamel sample. The dilatometer samples were produced using the raw enamel paste. These small samples cannot be produced in factory or pilot line furnaces but have to be fabricated with a laboratory procedure. The enamel paste was poured in an Al2O3 crucible, and placed in an oven for 2 hours at 160°C to remove the solvent. Then, the crucible was placed for 30 minutes at 350°C in a furnace to eliminate the resin, leaving the remaining mineral powder. The coarse powder had been grounded and filtered using a 63-μm filter. The fine powder was poured in a mold and compressed with 15 kN force. The obtained beam was sintered by heated up for 1 hour to reach 650°C, then, the temperature is held for 10 minutes. Finally, the specimen was slowly cooled down to room temperature. The sintering conditions have been chosen such that the visual aspect of the bulk samples was comparable to the enameled glasses.

### 3.5 Interdiffusion with glass substrate

The diffusion between the enamel n°2 thick film and the SLS substrate were measured using TOF-SIMS 5 (ION-TOF GmbH, Münster) using a 60 keV Bi3⁺ to obtain a positive spectra. The pixel density was 1024 × 1024 over 50 × 50 μm. The charge compensation flood gun was kept on during the analysis. The diffusion was investigated onto mechanically polished stack cross-section. Therefore, a chemical distribution mapping of the surface could be reconstructed, providing structural information of the layer, with a high spatial resolution of approximately 100 nm. The polished cross-section of the enameled glass was prepared with an automated polishing procedure employing ethanol to reduce alkaline leaching during sample preparation. The technique consists in bombarding the sample surface under primary ions and analyzing the intensity of secondary ions emitted from the surface.

The interdiffusion profiles are obtained by averaging the pixel counts of each ion along the length of the film (vertical axis) of the spatial distribution image and representing the average counts in function of the thickness of the stack (horizontal axis). The typical spatial distribution image of element over the enameled glass cross-section is represented Figure 5. Microscope pictures of the enamel n°2 deposited onto the Borosilicate Eagle 2000 glass substrate: (a) Reflection image from the enamel surface presenting the cracks in the enamel layer, (b) Reflection images from the glass side presenting the glass chips (Figure 6b).

### 4 RESULTS

The thermoelastic properties of three standard enamel pastes used for automotive glasses are investigated with the curvature measurement set-up. The pastes references are enamel n°1, enamel n°2, and enamel n°3. The average thickness of the enamel thick films, measured by surface profilometer, is 12.5 ± 0.5 μm. The typical evolution of stresses in the enamel film deposited onto thin glass substrates during the cooling phase of the sample temperature inside the furnace is presented (Figure 2a). For each of the three enamel pastes, the slope $\sigma_{\text{film}}/\partial T$ is measured onto V95, SLS and CS77 thin glass substrates and graphically represented in function of the substrate CTE (Figure 2). The evolution of the slopes $\sigma_{\text{film}}/\partial T$ measured on a set of different substrates recovered with an enamel paste varies linearly with the substrate CTE, verifying the Equation (3). The CTE and biaxial modulus values of enamel suppliers determined by curvature method are presented Table 2. The amount of residual stress present in the layers as deposited onto green SLS float glass, the substrate employed for automotive glasses, can be calculated using the Equation (2) under the assumption that all the residual stresses in the coating are due to the CTE mismatch. The residual stress in the film is proportional to the CTE mismatch between the glass substrate and the layer and the biaxial modulus of the film. For the glass substrate recovered with enamel, the
The glass transition temperature of the enamels n°1 to n°3, measured by DSC (Linseis L75 Platinum Series), is respectively 465 ± 5°C, 495 ± 5°C and 485 ± 5°C. The CTE of the green SLS glass substrate is 89 ± 1 × 10⁻⁷ K⁻¹. The amount of porosities present in the different enameled glasses is evaluated via SEM images (GeminiSEM 500 Yeiss) on the cross-section of polished samples (Figure 3). The enamel n°2 has also been deposited onto AF45 (CTE = 45 × 10⁻⁷ K⁻¹) and Eagle 2000 substrate (CTE = 32 × 10⁻⁷ K⁻¹). Glass chips are observed in the glass by episcopic microscopy (HIROX Digital microscope KH-7700 equipped with a MXG-5040RZ lens).

Figure 2: Curvature measurement: A, Evolution of the residual stress in the enamel n°2 film of 12.5 µm deposited onto thin (700 µm) V95 glass substrate upon cooling, B, (Slope(σ film vs T cool) vs Substrate CTE for different enamel layers (when not visible, error bars are smaller than the point) [Color figure can be viewed at wileyonelibrary.com]

Figure 3: SEM analysis of the enamel cross-section surface deposited onto SLS glass substrate: A, enamel n°1, B, enamel n°2, C, enamel n°3

Table 2: Measurement of CTE and biaxial modulus of enamel suppliers by curvature method, and residual stress calculation using Equation (2)
the glass chips are starting at the enamel-glass interface (Figure 4). SEM analysis of the enamel cross-section surface deposited onto SLS glass substrate: (a) enamel n°1, (b) enamel n°2, (c) enamel n°3 (Figure 4).

Higher magnification reflection images on the enamel deposited on the borosilicate Eagle 2000 demonstrate that the enamel layers present a network of cracks, initiated in the layer and propagating further to the glass substrate (Figure 4A). The cracks in the glass substrate are then forming a network of glass chips, as shown by the microscope images (Figure 5B). The thermoelastic properties of the enamel n°2 thick film measured by curvature technique are compared to the CTE measured by dilatometer on a bulk enamel sample (Table 3). The elongation of the dilatometer beam has been measured between 20°C and 620°C, and the CTE was determined between 200°C and 400°C. Additionally, the glass
The transition temperature of the CS77 and V95 glass substrate was measured by dilatometers; the values are 636 ± 5°C and 546 ± 5°C respectively. The interdiffusion of elements at the interface between the glass substrate and the enamel has been investigated to provide explanations for the difference in CTE between the enamel bulk sample and the enamel thick film deposited onto glass. The diffusion of elements can modify locally the layer’s properties, such as CTE, and can induce residual stresses. Therefore, the spatial distribution of the different elements, investigated on the polished cross-section, has been investigated by time-of-flight secondary ion mass spectrometry (TOF-SIM) technique. The cartography of the spatial distribution of sodium ions on the enameled glass cross-section is presented in Figure 5. Microscope pictures of the enamel n°2 deposited onto the Borosilicate Eagle 2000 glass substrate: (a) Reflection image from the
dubbed.TAB.3 | Coefficient of thermal expansion of enamel n°2 measured by curvature and dilatometer techniques

| Enamel n°2 | Curvature | Dilatometer |
|------------|-----------|-------------|
| CTE (10⁻⁷ K⁻¹) | 64.1 ± 2.3 | 88.5 ± 0.1 |

**FIGURE 6** Chemical analysis on the enameled glass cross-section by TOF-SIMS technique: A. Element interdiffusion length between the enamel and the glass substrate. B. Cartography of the spatial distribution of sodium ions [Color figure can be viewed at wileyonlinelibrary.com]
enamel surface presenting the cracks in the enamel layer, (b) Reflection images from the glass side presenting the glass chips (Figure 6b).

The interdiffusion diffusion profiles of the different alkali elements and the silicon ions are presented on Figure 5. Microscope pictures of the enamel n°2 deposited onto the Borosilicate Eagle 2000 glass substrate: (a) Reflection image from the enamel surface presenting the cracks in the enamel layer, (b) Reflection images from the glass side presenting the glass chips (Figure 6a).

Finally, the mechanical properties of the different enamel samples have been characterized by Ring On Ring (ROR) biaxial flexure testing onto 3.85-mm thick enameled glasses. The Weibull distribution plots of the different enamel suppliers are presented in Figure 5. Microscope pictures of the enamel n°2 deposited onto the Borosilicate Eagle 2000 glass substrate: (a) Reflection image from the enamel surface presenting the cracks in the enamel layer, (b) Reflection images from the glass side presenting the glass chips (Figure 6).

Chemical analysis on the enameled glass cross-section by TOF-SIMS technique: (a) Element interdiffusion length between the enamel and the glass substrate, (b) Cartography of the spatial distribution of sodium ions (Figure 7), while the Weibull parameters are reported in Table 4.

5 | DISCUSSION

The evolution of the stresses in the different enamel films upon cooling is relatively linear during the cooling phase, indicating the absence of significant structural modification such as recrystallization or stress relaxation. The slope \( \frac{\partial \sigma_{\text{film}}}{\partial T} \) is measured in the most linear part of the curve, between 150°C and room temperature. Additionally, since the curvature is recorded each for 70 seconds, the measurement of the slope is more accurate at lower temperature due higher number of points available, as the cooling rate decreases over time (Figure 1b). Then, the evolution of the slopes \( \frac{\partial \sigma_{\text{film}}}{\partial T} \) measured on a set of different substrates recovered with an enamel paste varies linearly with the substrate CTE, verifying the Equation (3). The value of the coefficients of determination \( R^2 \) for the linear regressions provides good confidence on the value of the enamel thermoelastic properties measured with this technique. The biaxial modulus and coefficient of thermal expansion of the enamel n°2 are 53.1 ± 1.4 GPa and 64.1 ± 2.3 × 10⁻⁷ K⁻¹ respectively. In the literature, the value of Poisson’s ratio for similar bismuth zinc borosilicate glass frits range between 0.25 and 0.33. The value of the Young’s modulus of the enamel n°2 measured by curvature technique is approximately 40 GPa, by using a Poisson’s ratio of 0.27. In the literature, the average Young’s modulus of the enamel n°2, measured by nanoindentation technique, has been reported to be 96.4 ± 27.1 GPa. The value of the

| Enamel   | \( \sigma_0 \) (MPa) | \( m \) |
|----------|----------------------|--------|
| Enamel n°1 | 150.1 (151.6, 148.7) | 34.6   |
| Enamel n°2 | 143.8 (141.5, 146.1) | 25.6   |
| Enamel n°3 | 118.9 (117.2, 120.6) | 22.6   |

**TABLE 4** Weibull parameters: the characteristic strength (\( \sigma_0 \)), unbiased Weibull modulus (\( m \)). The values in the parenthesis represent a 95% confidence interval for N specimens.

**FIGURE 7** Weibull distribution plot of the different enamel suppliers [Color figure can be viewed at wileyonlinelibrary.com]
Young’s modulus determined with the two techniques differs significantly. The main difference between the two techniques relies in the size of analyzed volume for the measure of the Young’s modulus. The average biaxial modulus of the complete layers, measured with curvature measurement technique, comprise the contribution of the porosities present into the layer’s mechanical properties. The effective elastic moduli are directly affected by the amount of porosities present in the layers, as demonstrated by Equation (4). The nanoindentation technique probes the surface with micrometric load, however, the influences of the underlying porosity are negligible, resulting in elastic values very similar to the value of the fully dense material. Therefore, the comparison of the results obtained by the two techniques indicates the presence of a significant porosity ratio in the enamel layers. The porosity ratio in the enamel film, calculated using Equations (3) and (4), with $E_0$ as the nanoindentation Young’s Modulus and $E$ as the curvature technique Young’s modulus, is approximately of 26%. In Table 2, the value of coefficient of thermal expansion for the enamel n°1 and n°2 are very similar while the value for enamel n°3 is significantly higher. The glass frit chemistry of the enamels n°1 and n°2 is probably very similar, while the enamel n°3 has probably a significantly different composition, based on the respective CTE value. However, the glass transitions of the three enamel references are in relatively similar temperature range. The enamel n°1 and n°3 present similar values of biaxial modulus while the enamel n°2 has a significantly lower value. The SEM analysis of the cross-section of the enamelled glasses, Figure 3, demonstrates that the enamel n°2 has higher porosity ratio compared to the two other enamel references. Therefore, the difference of elastic properties between the enamel suppliers probably arises from different porosity fraction, and amount of pigments. The amount of organics present within the paste, the size of the glass frit, and the glass transition of the frits are expected to have an influence on the pore fraction. The enamel n°3 shows glass frits particles with smaller size (as visible in Figure 3). As the curvature in function of the temperature measurements shows a good linearity upon cooling, it is assumed that the residual stresses building up in the enamel layer are mainly due to the CTE mismatch between the enamel and the substrate, resulting in thermal stresses. The film is attached by the interfacial cohesion to the underlying substrate. The strain of the complete stack is almost equal to the substrate strain alone, since the substrate thickness is almost infinite compared to the film thickness. As a result, the substrate imposes his strain to the film. The SLS glass substrate, having a larger CTE value than the enamel film, shrinks more upon cooling than the isolated film, resulting in compressive residual stresses in the film. On the other hand, tensile residual stresses in the enamel layer can be generated upon cooling when deposited onto a substrate with lower CTE value compared to the film. The residual stress in the film, calculated with Equation (2), is proportional to the CTE mismatch between the glass substrate and the layer and Young’s modulus of the film. Therefore, an important CTE mismatch, the substrate having the higher CTE, coupled with a high Young’s modulus provides high compressive stresses in the enamel upon cooling down. The enamel n°1 has the highest calculated compressive stress value, while the enamel n°3 has almost twice less compressive stress. The mechanical performances of the three enamels are ranked in the same order than the amount of calculated compressive stress present in the layers. The larger defects present in the enamel n°2 compared to enamel n°1 decrease the mechanical performance and the amount of compressive stress in the layer. These observations indicate that a high Young’s modulus and a high CTE mismatch with the glass substrate, inducing compressive stress, have a beneficial effect on the mechanical performance of the complete system by preventing the propagation of cracks at the defect locations. However, an excess in compressive stresses would probably lead to the failure of the enamel by delamination. Therefore, the critical maximum value of compressive stress should be further investigated in order to define the optimum stress value for the enamel. The positive action of compressive residual stresses in the film on the mechanical performance of the complete system could be further demonstrated by the opposite effect of the tensile residual stresses applied to the film, leading to glass chips in the glass substrate initiated by cracks in the enamel film. The fracture toughness of the SLS float glass, the AF45 and the Eagle 2000 substrates are assumed to have similar values. The amount of cracks at the interface between the film and the glass substrate increases with the amount of tensile stress present in the enamel layer. The enamel deposited onto the borosilicate Eagle 2000, the substrate with the lowest CTE, presents a significant increase in the amount and size of cracks compared to the borosilicate AF45. The CTE of the enamel film, measured by the curvature technique, is compared to CTE of bulk enamel samples analyzed by the dilatometer. The elongation of the bulk sample was measured between 20°C and 620°C. Therefore, the dilatometer samples have undergone a first sintering at 650°C for sample preparation and a second heating phase until 620°C for the measurement of the CTE. Typically, the production of automotive glasses requires a firing time of 180 seconds at a furnace temperature of 700°C. However, in the case of the dilatometer, the sample preparation and measurement required significantly longer time firing due to the sample thickness. The mineral part of the enamel is composed of CuCr2O4 pigments and Bi2O3–B2O3–ZnO–SiO2 glass frits. After firing, Zn2SiO4 and Bi2Si2O7 are formed in the Bismuth-rich glass frits. The heat flow absorbed during the firing by the dilatometer...
beam and the enamel layer onto glass is different. Therefore, the difference of enamel CTE value, measured by the two techniques, is associated with different crystalline ratio and crystalline structures in the thick film and the bulk sample. Additionally, the diffusion occurring in enameled glasses between the film and the substrate is absent for bulk dilatometer samples. As a result, the CTE values measured by curvature techniques is more representative of the standard automotive glasses, compared to the dilatometer techniques, since the enamel structure, thermal history and interdiffusion with the substrate is comparable to the final product. The main drawbacks of this technique rely in the indirect determination of the film CTE and biaxial modulus. The presence of interdiffusion diffusion profiles of the different elements have been demonstrated by the TOF-SIMS measurement. However, the quantitative analysis of element concentration along the diffusion profiles is complicated due to the effect of the matrix. Indeed, the local structure and chemical composition of the matrix material influences the intensity of the emitted secondary ion regardless of the actual element concentration.22,26 Another limitation of the curvature technique is the differences in inter-diffusion of elements between the enamel and the thick glass substrates, having different composition. Additionally, the glass transition temperature of the CS77 substrate is 90°C higher than the V95 substrate. Higher $T_g$ value of the substrate induces smaller amount of interdiffusion. However, the evolution of the slopes $\partial\sigma_{film}/\partial T$ in function of the substrate CTE is relatively linear, according to the value of the coefficients of determination $R^2$. Therefore, the amount of interdiffusion between the enamel and the set of substrates is assumed to be relatively similar. As a result, there is a good confidence on the CTE and biaxial modulus values measured on the different enamel thick films using the curvature technique.

6 | CONCLUSION

In this work, the coefficient of thermal expansion and the average biaxial modulus of enamel thick films have been simultaneously measured by the curvature technique. The advantage of this method relies in the measurement of the thick film properties as deposited onto a substrate, while standard methods such as dilatometer requires a bulk sample for the analysis. The thermoelastic properties of enamel thick films differ from the value measured on a bulk material having the same initial chemistry. The interdiffusion of elements with the substrate modifies the average CTE, while the amount of porosities present in the enamel film has been found to greatly influence the biaxial modulus value. The interdiffusion of elements between the enamel film and the glass substrate has been demonstrated with TOF-SIMS technique. Compressive residual states in the different enamels reference have been calculated from the measured thermoelastic properties, ranging between $-76.9 \pm 26.6$ and $-42.4 \pm 7.6$ MPa. The mechanical performances of the three enamels, investigated by ROR technique, were found to be proportional to the amount of calculated compressive stress present in the enamel. On the contrary, as tensile residual stresses are applied to the enamel film, cracks were observed in the film, leading to glass chips in the glass substrate, which weakens the mechanical properties of the stack. Therefore, a high Young’s modulus for the enamel thick films associated with an important mismatch of the coefficient of thermal expansion between the enamel film and substrate, the film having the lowest value, has been found to increases significantly the mechanical performance of the stack.

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