Measurement of the mechanical properties of silver and enamel thick films using nanoindentation

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Abstract
Analyzing material properties of thick film multilayers deposited onto soda-lime silicate glass raises several challenges since these layers can exhibit complex multiphase microstructures. The mechanical properties of sintered silver and glass enamel thick films have been investigated using nanoindentation methods to provide deeper understanding of the composite stack in-service failure mechanisms. The spatial distribution of the Young’s modulus and hardness have been studied on the cross section of the layers to avoid the influence of surface roughness and underlying glass substrate. The apparent indentation fracture toughness of the layers has been evaluated via SEM and high-resolution surface topography images of the hardness imprints. A modified Berkovich indenter has been employed to study the elastic and plastic deformation regimes while the fracture deformation regime has been investigated using a cube-corner indenter. In the enamel layer, copper chromite spinel pigments were found to provide a beneficial effect on the films mechanical performance due to their significantly higher elastic, hardness, and toughness properties compared to the surrounding amorphous phase. The amorphous phase of the enamel layer and the glass substrate has comparable mechanical properties, while the fracture toughness of sintered silver is higher, partially explaining the failure initiation in the enamel layer.

KEYWORDS
enamel, fracture toughness, hardness, nanoindentation, sintered silver, Young's modulus

1 | INTRODUCTION

Enamel and silver thick film multilayers deposited onto soda-lime silicate glass are of great interest in many applications, such as automotive and architectural glass. However, the layers can introduce bottlenecks in the designing process. The glass enamel, composed of a low-melting glass frit containing an oxide pigment, is required for UV protection and decorative purposes. For specific products, an additional sintered silver layer is applied for the electrical functionalities. However, the main drawback of thick films is their weakening effect on the mechanical strength of the glass substrate. 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 aggregate in the enamel film. Then this failure propagates to the glass substrate. Until now, the effect of an additional silver thick film on the robustness of enameled glasses has not been investigated. The characterization of the mechanical behavior of thick films is essential to provide a deeper comprehension on the in-service failure mechanisms. Despite the
abundance of studies on the material properties of sintered silver, there remains many underexplored features concerning the mechanical properties of glass enamel; therefore, the enamel fracture toughness, Young’s modulus, and hardness are presented in this paper. Fracture toughness is a fundamental parameter to understand fracture failure, since it indicates the amount of stresses required to propagate a pre-existing flaw.

The mechanical behavior can easily be assessed by applying a local deformation onto a small volume of material. The scope of this paper is the characterization of the mechanical properties of the stack, consisting of the sintered silver, glass enamel thick film, and the glass substrate using nanoindentation methods. The advantage of this widely used and inexpensive technique resides in the direct quantitative determination of the local Young’s modulus and hardness by analyzing the load-displacement curves. Furthermore, a great advantage of indentation lies in the ability of mapping the surface properties by probing it at numerous points, with a maximal resolution reaching the submicrometer scale. Therefore, in the first part of this paper, the spatial distribution of the Young’s modulus and hardness are studied on the cross section surface of the layers, using a modified Berkovich indenter. The modified Berkovich indenter has the same projected area as the Vickers indenter at any given indentation depth. The measurement on the cross section prevents the influence of surface roughness and underlying glass substrate. This surface mapping permits the characterization of the properties of the different phases constituting the enamel film.

In the second part, the apparent indentation fracture toughness of the layers has been evaluated from SEM analysis and high-resolution surface topography images of the hardness imprint. Furthermore, the imprints have been realized by a cube-corner indenter, due to the presence of cracking thresholds.

The determination of the fracture toughness by indentation consists in measuring the lengths of the cracks at the corners of the hardness impression. In the case of formation of long half-penny cracks, the Lawn-Evans-Marshall (LEM) model provides a simple relationship between the fracture toughness and the radial-median crack length. Alternative methods such as the micro-cantilever bending method has proven to be suitable to characterize fracture toughness for sintered silver. The advantage of this method is the absence of the influence of the density, porosity, or structure of the materials on the measurement. However, since this technique requires relatively complex sample preparation, nanoindentation technique was preferred.

Finally, the comparison of the layer’s mechanical behavior with the fractography results are discussed to define the most influencing material and physical properties in order to provide a deeper comprehension in the actual in-service failure mechanisms of the composite stack.

2 | EXPERIMENTAL PROCEDURE

The substrate consisting of commercial soda-lime silicate glass (SGG Planiclear®, Saint-Gobain) with a typical composition of 73 wt% SiO₂, 14 wt% Na₂O, 8 wt% CaO, 4 wt% MgO. 1 wt% Al₂O₃ was used in this study. Commercially available enamel (14 501, Ferro) and silver (SP 1989, Ferro) pastes for automotive tempered glass were applied onto the soda-lime silicate glass by screen-printing technique, using a plain weave mesh constituted of 48 μm diameter with 90 threads per cm, resulting in an ink volume of 19 cm³/cm². The deposited silver and enamel pastes are dried at 250°C for 180 seconds in order to eliminate the solvents, reducing the risk of porosity after the sintering process. Then, the complete stack undergoes a thermal treatment in a furnace at 700°C for 180 seconds in order to remove the remaining resin, sinter the silver layer, 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 composition of the enamel and silver pastes 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 silver layer has a typical composition of 93 wt% silver and 7 wt % bismuth-zinc borosilicate glass frits. The enamel has a typical composition of 80 wt% bismuth-zinc borosilicate glass frits and 20 wt% CuCr₂O₄ pigments particles. The film thickness and surface roughness were measured using a MarSurf M 400 surface profilometer (Mahr GmbH). Fractographic analysis was undertaken onto samples broken by three-point bending technique. Visual inspections of the samples enable the determination of the location of the fracture initiation and the type of failure; while the original defect located in the middle of the fracture mirror was investigated using a Leo 440i SEM with INCAx-sight detector from Oxford instruments.

2.1 | Young’s modulus and hardness

Nanoindentation measurement was performed onto sintered silver layer, enamel layer, and the glass substrate with a Hysitron TI 950 Tribo-Indenter. Indentation measurement took place on the polished cross section of the layers, prepared with an automated polishing procedure employing ethanol to reduce alkaline leaching during sample preparation. Indeed, measurement on the cross section surface avoids the contribution of the substrate Young’s Modulus on the analyzed properties, and the significant influence of the relatively high roughness on the layers top surface compared to the indentation depths. A modified Berkovich tip was used as indenter for the characterization.
of the layers Young's modulus and hardness. The measurements were done with load-control indentation where the loading rate is 200 μN/s\(^{-1}\) for 5 seconds, the maximum load is 1 mN with a dwell time of 2 seconds, and the unloading rate is −200 μN/s\(^{-1}\) for 5 seconds. An automated indentation procedure for the mapping of the surface mechanical properties has been developed, consisting in 20 lines and 14 columns with a separation distance between indents of 1 μm. The spatial distribution of the Young's modulus and hardness on the cross section surface was obtained from the analysis of the load-displacement curves arising from the indentation mapping.

During the indentation, the displacement of the tip, the load \(F\), and the contact stiffness \(S\) are the three quantities measured in function of time. The plain strain modulus \(E^*\) and hardness \(H\) are obtained by using a model. The contact stiffness corresponds to the derivative of the load with respect to tip displacement in the elastic part of the curve, at the beginning of the unloading step. An advantage of indentation lies in the ability of assessing several mechanical properties, such as \(E^*\) and \(H\), by analyzing the load-displacement curves. Therefore, it is not required to have a hardness impression image of the indent, facilitating the submicrometer scale analysis. The most frequently used model for the determination of \(E^*\) and \(H\) is the Oliver and Pharr model.\(^9\) This model provides a value of \(E^*\) as a function of the indentation depth. The contact depth can be calculated with the following formula:

\[
h_c = h - \epsilon \frac{F}{S}\]  

(1)

with \((h_c)\) the contact depth, \((h)\) the total indentation depth, \((\epsilon)\) a numerical factor fixed in this study at 0.75 [5], \((F)\) the applied load, and \((S)\) the contact stiffness. The projected contact area \((A_c)\) for a perfect Berkovich tip is given by:

\[
A_c = K h_c^2
\]  

(2)

\((K)\) is a geometric factor depending on the shape of the tip and is equal to \(K = 24.5\) for a modified Berkovich tip and \(K = 2.6\) for a cube-corner tip. Since diamond indenters usually suffer from tip imperfections, the tip area function \(A_c\) of the modified Berkovich and cube-corner indenters have been calibrated onto fused silica. The calibration consists in 200 indents at 22 different forces from 0 to 10 mN. In order to take into account the tip defect, the indenter area function can be calculated, based on the reference samples properties, as follow:

\[
A_c = Kh_c^2 + K_1h_c + K_2h_c^{1/2} + K_3h_c^{1/4} + \ldots + K_8h_c^{1/128}
\]  

(3)

where \(K_0, \ldots, K_8\) are constants determined by curve-fitting procedures.\(^9\)

The reduced modulus \((E_r)\) can be calculated using Sneddon's equation as:

\[
E_r = \frac{\sqrt{\pi} \frac{S}{2\beta}}{\sqrt{A_c}}
\]  

(4)

The factor \(\beta\) depends on the tip geometry and is equal to 1.034 for a triangular-based tip such as a Berkovich tip. The reduced modulus is a combination of the elastic properties of the sample and of the tip:

\[
\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu^2}{E}
\]  

(5)

\((E_i)\) is Young's modulus and \((\nu_i)\) the Poisson's ratio of the material composing the indenter tip. Indentations tips are made of diamond; therefore, \(E_i = 1141\) GPa and \(\nu_i = 0.07\). The plain strain modulus of the sample can be determined for each value of indentation depth \((h)\) or contact height \((h_c)\) as:

\[
E^* = \frac{E}{1 - \nu^2}
\]  

(6)

The drawback of nanoindentation, as many other techniques probing at submicrometer scale such as the picosecond laser ultrasonics\(^18\) and Brillouin’s scattering,\(^19\) resides in the fact that it is an indirect measurement of elastic properties and does not give direct access the Poisson’s ratio.

The hardness \((H)\) can be determined using the following formula:

\[
H = \frac{P_{\text{max}}}{A_c}
\]  

(7)

where \((P_{\text{max}})\) is the peak indentation load and \((A_c)\) is the projected area of the hardness impression.

### 2.2 | Fracture toughness

Nanoindentation is a widely used method to measure fracture toughness at submicrometer scale.\(^12\) The determination of the fracture toughness by indentation consists in measuring the lengths of the cracks at the corners of the hardness impression. The fracture toughness of the glass substrate and the layers has been determined using a diamond cube-corner indenter, due to the presence of cracking thresholds. Indeed, in most brittle materials, below a defined load threshold which is material specific, the cracking does not occur.\(^12\) Fortunately, this load of cracking threshold can be significantly reduced by employing cube-corner indenter because of the sharper tip which applies greater volumetric displacement compared to the Berkovich indenter.\(^10,20\)

The maximum load used to measure fracture toughness was 10 mN with a dwell time of 2 seconds for the glass and enamel. Since sintered silver layer is a much softer material
than enamel and glass, the maximum load is fixed to 1 mN to generate comparable hardness imprint size. An automated indentations procedure has been set for the measurement of the layers and glass toughness, consisting in the generation of 30 indents along a line parallel to the glass surface in each analyzed materials. Each indent is separated by 10 micrometers to avoid any interactions between two indents. The hardness impression, crack morphologies, and the length of radial‐median cracks are evaluated on high‐resolution surface topography images using the indentation tip, and by SEM images. The fracture toughness was evaluated by estimating the length of indentation cracks. In the case of formation of long half‐penny cracks (c/a → 1) in a stress‐free material, the LEM model provides a simple relationship between the fracture toughness in the stress‐free material ($K^0_C$) and the radial‐median crack length ($c_0$):

\[ K^0_C = a \left( \frac{E}{H} \right)^{1/2} \left( \frac{P_{\text{max}}}{c^3} \right)^{3/2} \]  

(8a)

where $K^0_C$ is the fracture toughness in the stress‐free material, $(P_{\text{max}})$ is the maximum indentation load, $(H)$ is the hardness, $(E)$ is the Young's Modulus, $(c_0)$ is the crack length, and $(a)$ is an empirical constant depending on the geometry of the indenter. In this study, the values of $(H)$ and $(E)$ measured with a modified Berkovich indenter are used in this formula. The long half‐penny cracks must be at least twice the half diagonal of the indent. For cube‐corner indenters, the value of the geometric constant $a$ used in this study is 0.040. In the literature, the value of $a$ ranges between 0.036 and 0.040.8,12

Residual stresses are usually generated in thick film upon cooling phase during the manufacturing process, from the mismatch in the coefficients of thermal expansion between different layers and substrate. Such stresses logically modify the films cracking behavior. Under the influence of residual stresses ($\sigma_r$), the initial crack in the film will grow to a new equilibrium radial‐median crack length ($c$) as the surface undergoes the same maximum indentation load as the unstressed film having an equilibrium radial‐median crack length ($c_0$). At equilibrium, a composite stress intensity is applied to the radial‐median crack tip, described by the apparent indentation fracture toughness ($K_C$):20,21

\[ K_C = a \left( \frac{E}{H} \right)^{1/2} \left( \frac{P_{\text{max}}}{c^3} \right)^{3/2} \]  

(8b)

\[ K_C = K^0_C + \psi \sigma_r c^{1/2} \]  

(8c)

where $(\sigma_r)$ is the surface residual stress value and $\psi$ is a crack‐geometry factor. For radial‐median median cracks, $\psi = 1.26$. The first term of the expression is the contribution of the maximum indentation load to the crack tip stresses while the second term concerns the contribution of the film residual stresses. For a film under tensile stresses, the second term is added to the first one, while it is subtracted in the case of compressive stresses. Since stresses are present in the final product, the comparison of the layer apparent indentation fracture toughness is sufficient to provide deeper understanding in the actual in‐service failure modes of the composite stack. The indentation microfracture method sometimes is criticized since it is not suitable for a precise evaluation of the true fast fracture toughness.22,23 Indeed, the methods assume ideal geometries of cracks using an empirical calibration constant. The measurement error on the estimation of crack length and irregular fracture behavior can result in accuracy on the toughness evaluation within about ±40%.10,22 Therefore, this method enables an estimation of the fracture toughness rather than a precise quantitative measurement. But it nevertheless allows the correlation with the fracture failure, providing a better insight into the failure mechanism.

3 | RESULTS AND DISCUSSION

3.1 | Fractographic observation

Fractographic analysis has been conducted on 30 thermally tempered samples broken by three point bending to investigate the main type of defects leading to the failure of SLS glass recovered with silver and enamel thick films. The bending tests have been conducted at a stress rate of 2.0 ± 0.5 MPa/s and the length of the support span is 100 mm. Visual inspections of the samples enabled the determination of the location of the fracture initiation and the type of failure, such as surface or volume flaws. The fracture mirrors were analyzed using SEM to determine the fracture origin, which is located in the middle of the mirror (Figure 1). In Figure 1B, the top white layer is the sintered silver, the middle layer is the enamel, and the bottom darker layer is the glass substrate.

SEM fractographic analyses have revealed that fracture originated in the enamel layer and more especially the region near the interface with sintered silver. The crack propagates from the enamel to the glass substrate, creating the fracture mirror. The different failure location and the number of specimens presenting this type of failure are presented in the Table 1.

These results are in good agreement with previous studies on the degradation of the soda‐lime silicate glass strength after enameling, demonstrating that the fracture is initiated in the enamel layer.1,2 The observation of the SEM pictures has demonstrated that larger flaws are present in the silver and enamel layers compared to the glass surface. The defects present in the enamel consist in porosities and pigment aggregation. Sintered silver microstructure also contains
porosities, resulting from an incomplete sintering or from gas bubbles derived from the elimination of the organic content present in the deposited pastes. In fracture mechanics, the failure of a material can be understood by investigating the main influencing parameters consisting in the material mechanical properties such as fracture toughness, the defect morphology, and the sum of stress applied to this defect resulting from residual stresses and applied load.

3.2 Young's modulus and hardness

Nanoindentation took place onto the mechanically polished cross section since the measurement is not feasible on the layers top surface due to the relatively high surface roughness compared to the indentation depths. The layers thickness and top surface roughness have been measured by surface profilometer. The arithmetical mean roughness (Ra) of the enamel and sintered silver is $0.5 \pm 0.06$ and $1.01 \pm 0.02$ μm, respectively. The average thickness of the enamel and sintered silver is $12.5 \pm 0.5$ and $7.9 \pm 0.4$ μm, respectively.

The load-displacement curves, resulting from the indentation in the layers and glass, are plotted in Figure 2. An indentation mapping, consisting in 20 lines indents and 14 columns indents enable the measurement of the local Young's modulus and hardness of the system. Each indent is separated by 1 µm in order to ensure sufficient inter-indent distance and avoid any interactions. Hence, the scanned surface is $280 \, \mu m^2$. The Young's modulus and hardness can be measured from the load-displacement curves at each indent location. A surface topography image of the layers cross section after indentation has been produced using the indenter tip as a surface profilometer (Figure 3A), revealing the presence of the nanometre size indentation mapping pattern in the enclosed rectangle. The spatial distribution of the reduced modulus and hardness of the sintered silver, enamel, and SLS glass were obtained from the analysis of the indentation mapping performed on the cross section surface (Figure 3C,D).

A typical SEM cross section image of the layers shows their microstructure (Figure 3B). The top layer is the silver layer, the middle layer is the enamel while the bottom part is the glass substrate. The enamel microstructure is composed of bismuth-zinc borosilicate glass frits surrounded by micrometer size copper chromite spinel pigments particles (CuCr$_2$O$_4$). The local granular phases with higher topography consist of the pigments, since it is the hardest phase. Indeed, during the preparation of the cross section by mechanical polishing, the pigment particles are less polished then the softer surrounding glass frits.

| Fracture origin               | Number of specimens |
|-------------------------------|---------------------|
| Interface enamel—silver       | 23                  |
| Enamel layer                  | 1                   |
| Undetermined                  | 6                   |
| Total                         | 31                  |
In both spatial distribution images, the upper dark blue band corresponds to the softer silver layer, the middle inhomogeneous band is the multiphase enamel and the lower band is the glass substrate. A comparison between the spatial distribution and surface topography images have demonstrated that the yellow and red areas in the enamel correspond to the pigments locations while the surrounding blue and green areas consist in the enamel glass frits. The higher topography of the pigment particles might introduces measurement errors by modifying the calculated projected contact area, resulting in an under estimation of the Young’s Modulus and hardness.

The results of the spatial distribution images are in correlation with the literature since spinel structures usually have higher Young’s modulus and hardness compared to typical glass compositions. For instance, the micromechanical properties of MgAl₂O₄ spinel with a grain size 0.5-5 μm have been evaluated by nanoindentation. The hardness values have been reported to range between 12 and 17 GPa while the Young’s modulus range from 140 to 240 GPa. The Young’s modulus, hardness, and Poisson’s ratio of soda-lime silicate glass have been reported as 70.0-76.1, 6.1, and 0.23 GPa, respectively. The Young’s modulus of the layers can be calculated from the measured plain strain modulus by using Poisson’s ratio values from the literature. The value of Poisson’s ratio used in the case of the enamel, composed of bismuth-zinc borosilicate glass frits, is 0.27. In the literature, the value of Poisson’s ratio for similar composition range between 0.25 and 0.33. For the sintered silver, the Poisson’s ratio of fully dense pure silver has been employed. In the literature, the average value of the Poisson’s ratio measured on the complete thick film has been found to decrease with the amount of porosities. However, in the case of nanoindentation, the size of the indents is smaller than the silver particles size. Furthermore, the mechanical polishing tends to close the open porosities by deforming the silver surface (Figure 3B). Therefore, locally, the indenter is in contact with the pure silver. The average values of the hardness and Young’s modulus calculated with the Poisson’s ratio for the different layers are summarized in Table 2. Additionally, the value of the enamel glass frit properties are obtained by selecting only the indent in the mapping performed on the amorphous phase. The Young’s modulus of pure silver has been reported to be 83 GPa.
However, the pores ratio reduces dramatically the Young’s modulus of sintered silver. Typical Young’s modulus values for sintered silver thick film measured by tensile testing and dynamic mechanical analyser with a porosity ratio of 30% have been reported as ranging from 15-25 GPa. The Young’s modulus measured by nanoindentation technique is relatively higher closer to the pore-free silver since it is a local surface measurement at the nanoscale on the silver particle. Hence, the local influence of the underlying porosity is observable but much lower than for other technique, such as, dynamic mechanical analyser since the Young’s modulus of the complete film is measured.

Additionally, in metals, such as silver, the mechanical polishing is expected to produce similar effects to shot peening treatment, producing compressive residual stress in the material by surface plastic deformations. The local plastic deformations probably induce a local densification which would increase the measured Young’s modulus and hardness.

Histograms representing the probability distribution of Young’s modulus and hardness for enamel and silver layers are presented on Figure 5.

The histogram plots results from the analysis of the indentation mapping data performed respectively on the enamel and silver layers. The red curve is the kernel distribution fit applied to the histograms. The histograms of the enamel, colored in yellow, suggest the presence of three distinct phases. Correlations between the spacial distribution images and the histogram strongly suggest that the third phase, having the highest hardness value, corresponds to the pigment particles. Furthermore, the phases 1 and 2 would then consist in two distinct types of glass frits. Shades of grey color in the amorphous phases surrounding the pigments particles on the SEM picture (Figure 3B) confirm that the enamel is constituted of several type of glass frits. The glass matrix in the enamel is composed of bismuth-zinc borosilicate, the white area suggests bismuth-rich borosilicate frits while the dark grey suggests zinc rich borosilicate.

The distribution fit of histograms of the sintered silver, in blue, is nearly Gaussian, suggesting the presence of a single major homogenous phase.

The Young’s modulus and hardness values of the layers are useful for the determination of the fracture toughness of the layers at a micrometer scale, since these parameters are required in the LEM model.

### Table 2

| Material                        | SLS glass  | Enamel (average) | Enamel (glass frit) | Sintered silver |
|--------------------------------|------------|------------------|---------------------|-----------------|
| Plain strain modulus, $E^*$ (GPa) | 86.7 ± 3.3 | 104.0 ± 29.3      | 90.1 ± 11.9         | 81.9 ± 36.4     |
| Young’s modulus, $E$ (GPa)     | 82.1 ± 3.1 | 96.4 ± 27.1       | 83.5 ± 11           | 69.25 ± 30.7    |
| Poisson’s ratio, $\nu$          | 0.23       | 0.27             | 0.27                 | 0.39            |
| Hardness, $H$ (GPa)            | 7.7 ± 0.2  | 7.5 ± 2.4         | 7.0 ± 2.4           | 2.12 ± 2.5      |
| Crack length, $c$ (µm)         | 1.89 ± 0.13| —                | 1.89 ± 0.11         | 0               |
| $K_C$ apparent (MPa $\sqrt{m}$) | 0.50 ± 0.08| —                | 0.53 ± 0.18         | —               |
| $K_C$ (MPa $\sqrt{m}$)—independent study | 0.75-0.7$^{+bc}$ | —        | —                  | 7.43 ± 0.95$^d$ |

*Data obtained by dynamic method and ultrasonic technique*

*Data obtained by Cantilever technique*

*Data by Vickers indentation*

*Data by Micro-cantilever technique*

### Figure 4

Cross section of the indented layers by FIB slice
understanding in the fracture failure, since it indicate the amount of stress required to propagate a pre-existing flaw.

The load-displacement curves, for the indentation in the layers and glass, are plotted on Figure 6. The peak penetration depth of the indent on the glass substrate and enamel layer at the glass frit location is nearly identical. Indeed, these two materials have similar hardness and Young's modulus.

In the enamel, the pigments are harder than the glass frit; hence, one can expect that under a given load, the peak penetration depth is smaller compared to the glass substrate. Since sintered silver layer is much softer material, the maximum load was fixed to 10% of the load used for glass and enamel, to generate comparable hardness imprint size for the silver layer.

High-resolution topographic image of the surface, before and after indentation, has been generated by scanning the surface with the indenter. Additionally, SEM images of the indentation at the same locations have been realized to enable a relatively accurate measurement of the crack length (Figure 7). The absence of radial-median cracks at the indents performed on sintered silver provides clear evidence of the higher fracture toughness compared to enamel and glass, but prohibits a quantitative comparison. Ductile materials, such as silver, have higher fracture toughness than brittle materials due to local plasticization at the crack tip under applied stress. The local plasticity reduces the stress intensity factor by decreasing the tip sharpness and therefore the crack geometry. Hence, higher amount of energy is required to generate and propagate cracks.

The soda-lime silicate glass substrate has a homogeneous microstructure ensuring high repeatability onto the radial-median cracks lengths resulting from the indentation. Concerning the enamel layer, an accurate measurement of the crack length was only possible via the hardness imprint located in the middle of the glass frit. Therefore, the enamel fracture toughness has been exclusively evaluated by images presenting these configurations. Long half-penny cracks (c/a \(>1\)) were observed at the edges of the hardness imprint for the indentation onto SLS glass and enamel glass frit; hence, the LEM model can be employed to evaluate the fracture.
toughness. The average fracture toughness of the enamel layer is relatively complex to assess due to the multiphase microstructure. The propagation of radial-median cracks from an indentation in a glass frit seems to be inhibited by the presence of the nearby pigments. Additionally, the absence of cracks on the hardness imprint, directly at the pigments location, arises from the higher fracture toughness and hardness of the pigments.

However, the pigments could introduce a local tensile residual stress field due to local mismatch in the coefficients of thermal expansion between pigments and glass frits, weakening the local enamel mechanical properties. Until now, the linear thermal expansion coefficients (CTE) of CuCr₂O₄ spinel pigments have not been investigated. Nevertheless, metal spinel generally has smaller CTE compared with the bismuth-zinc borosilicate glasses. Chromite spinels, such as MgCr₂O₄, Mn₁₂Cr₁₈O₄, CoCr₂O₄, NiCr₂O₄, or ZnCr₂O₄, have a CTE ranging from 6.8 to 7.5 x 10⁻⁶/K⁻¹. They have a CTE ranging from 6.8 to 7.5 x 10⁻⁶/K⁻¹. Bismuth-zinc borosilicates glasses such as glass with composition of 65 wt% ZnO, 25 wt% B₂O₃, and 10 wt% SiO₂ with extra 10 to 15 wt% Bi₂O₃ have a CTE ranging from 7.7 to 8.5 x 10⁻⁶/K⁻¹. For a given glass ceramic, when the particles have a lower thermal expansion coefficient than the surrounding glass matrix, compression residual stresses are developed on the precipitate upon cooling. Additionally, the matrix develops compressive radial-median stresses and tensile tangential stresses. In this case, the tensile tangential matrix stress components generate microcracking in the matrix which links the precipitates. In order to understand the influence of the pigments on the fracture toughness of the enamel, the mechanical properties of the pigments and the surrounding glass frit have been further investigated by nanoindentation (Figure 8).

A maximum load of 10 mN with a dwell time of 2 seconds has been applied for the indentation 1, while for the indentation 2-9, the maximum load has been set to 2 mN with a dwell time of 2 seconds.

The smaller size of the indentation at the pigments location (5-9) demonstrates the higher hardness of this phase compared to the glass frit. The indentation onto the glass frit (2-4) does not present radial-median cracks, except the indent at the location 4 where the radial-median crack is propagating in the direction of the centre of the glass frit. The absence of radial-median cracks at the other locations suggests that the peak load is below the cracking threshold. The presence of tensile tangential matrix stress components in the matrix would have triggered the propagation of cracks mainly in the direction of the pigments. Therefore, if a stress field exists in the glass matrix around the pigments, the amount of stress seems relatively low. As a result, the pigments seem to acts as a reinforcement phase increasing the enamel mechanical properties. Table 2 presents the results of the apparent indentation fracture toughness for the enamel, silver, and glass substrate. The value of the SLS glass measured by nanoindentation is in reasonably good agreement with the values reported in the literature considering the method typical measurement error.

The indenter acuity modifies the amount of plastic deformation; therefore, the reduced modulus and hardness measured with a modified Berkovich indenter might have a different value compared to a cube-corner indenter. This effect could affect the evaluated value of the apparent indentation fracture toughness. In Figure 8, indents 2 and 3 onto the glass frit of the enamel provide a value of the hardness with a cube-corner indenter since the indents does not present radial-median cracks. The Young’s modulus and hardness of the glass frit are 112.4 ± 6.4 GPa and 10.8 ± 0.34 GPa, respectively. The values measured with a cube-corner indenter are higher compared to the average measured with a modified Berkovich indenter, but remain in the range measure with a modified Berkovich indenter. Furthermore, the measurement is very localized and not representative of the complete layer since it is based on two values.

The mechanical polishing probably modifies the layers residual stresses state at the indented surface. In metals, such as silver, the mechanical polishing is expected to induce similar effects than shot peening treatment, producing compressive residual stresses in the material by surface plastic deformations. In brittle materials, such as enamel and glass, mechanical polishing probably releases locally the surface residual stresses by allowing local strain. This change in the residual stresses state at the indentation location modifies the apparent indentation fracture toughness. Nevertheless, a semi-quantitative comparison between glass and enamel is allowed because the fracture toughness measured by cantilever technique and by nanoindentation on SLS glass has a comparable value, considering the typical measurement error of the indentation method.
FIGURE 7  Topographic image using the indenter tip and SEM pictures of the indented surface for the different configurations on: (A,B) sintered silver, (C,D) enamel glass frit alone, (E,F) enamel glass frit with pigment, (G,H) pigment, (I,J) SLS glass
Furthermore, enamel and glass have a similar Young's modulus, hence the modification of the residual stresses at the polished surface is assumed to be in comparable range of order for both materials. Therefore, the polishing technique seems to have a relatively small effect on the residual stresses present in the layers.

Fractographic analysis has revealed that fracture originated in the enamel layer and more especially the interface with sintered silver. The value of apparent indentation fracture toughness of soda-lime silicate glass and enamel glass frit measured by nanoindentation is comparable. These results indicate that the fracture toughness of the enamel is not one of the critical parameters, due to its inability to explain that the cracks is always initiated in the enamel rather than in the glass substrate surface. However, the fracture toughness of sintered silver measured with micro-cantilever technique is one order of magnitude higher than fracture toughness of the SLS glass, due to the low-yield stress leading to plastic deformations. Therefore, a defect with a given size and geometry present in the sintered silver would be less critical than in the enamel or glass due to the layer's higher resistance of to crack propagation. The higher fracture toughness of sintered silver partly explains that the fracture origin is always located in the brittle materials of the composite stack, such as the enamel. SEM analysis of broken sample suggests that the silver and enamel layers have much larger defects, such as porosities or pigment aggregation compared to the glass surface. In fracture mechanics, the main influencing parameters in fracture failure are the fracture toughness, the defect morphology, and the sum of stresses applied to this defect. Therefore, further investigation of the residual stresses, defect size, and geometry present in the complete system would provide full comprehension of the failure mechanism of enameled glass.

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4 | Conclusion

In this work, the fractographic analysis undertaken on a two-layer composite system, composed of sintered silver and glass enamel thick films deposited onto a glass substrate, revealed that the fracture is initiated in the enamel layer, and more specifically at the interface with sintered silver layer. Larger flaws have been observed in the silver and enamel layers compared to the glass surface. The spatial distributions of the Young's modulus and hardness on the cross section surface of the layers have enabled the local characterization of the glass frits and pigments composing the multiphase microstructure of the enamel. The spinel pigments were found to have a significantly higher elastic, hardness and toughness properties compared to the surrounding amorphous phase, providing a beneficial effect on the mechanical performance of the enamel.

Soda-lime silicate glass and the glass frit in the enamel were found to have comparable values of apparent indentation fracture toughness. These results indicate that the fracture toughness of the enamel is not one of the critical parameters, due to its inability to explain that the cracks are always initiated in the enamel rather than on the glass substrate surface. Porosities in the sintered silver were found to locally reduce the Young's modulus and hardness, resulting in a lower mechanical performance compared to bulk silver. The absence of radial-median cracks at the indents performed on sintered silver provides clear evidence of the higher fracture toughness compared to enamel, but prohibits a quantitative comparison. The higher resistance of the silver against crack propagation partly explains that the fracture origin is located in the enamel, which is a brittle material. Full comprehension of failure mechanism could be achieved by further analysis of the layers residual stress profile and flaws characteristics, including the flaws size and morphologies.
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