Modeling of Vitreous Porcelain Enamel Mechanical Properties

Brad Potter, Nicholas Carbo
Case Western Reserve University
Department of Material Science and Engineering

Charles Baldwin
Ferro Corporation

The resistance of vitreous porcelain enamels to chippage, crazing, and fracture needs to be optimal for a wide range of applications. Experimentation was done to characterize the fundamental properties of thermal expansion and modulus of elasticity (Young's modulus) to provide inputs for finite element analysis (FEA) modeling of multi-coat enamels on actual ware. Results of strain-to-failure testing confirmed that the three variables most strongly affecting coating durability were the difference in thermal expansion coefficient between the enamel and steel, the Young's modulus of the enamel, and the thickness of the coating. The experimental results were used to generate FEA models to estimate the residual compressive stress state. These simulations allow the validity of standard models for thermal stresses in enamels on steel to be assessed as well as optimizing the enamel durability and facilitating the design of enameled ware.

Introduction

Porcelain enamel coatings are selected for use because of their heat resistance, hardness, and abrasion resistance to line oven cavities, water heaters, clothes washers, and bathtubs as well as on pan supports, cookware, architectural panels, and general industrial applications such as reactor walls. Despite being a brittle material, there is increasing expectations for the chippage, spall, and/or thermal shock resistance of the enamel.

The fracture resistance and residual compressive stress state of the coating has been studied as a bilayer composite with different test approaches since the early days of industrial enameling.[1, 2, 3, 4, 5] It is well established that the enamel's strength is from being in a state of residual compression that develops on cooling of the enamel.[6] The residual compression arises from the enamel having a lower coefficient of thermal expansion, α, then that of the steel base layer.[7] For a single layer ground coat that is only on one side of a steel strip, the following can be used for a uniform compressive stress in the enamel because of the differences between the coefficient of expansion of the metal and enamel:

$$\boldsymbol{\sigma_e^c = \left[\frac{1}{\left(\frac{t_e}{t_s}\right)\left(\frac{E_e}{E_s}\right)+1}\right] E_e \Delta\alpha \Delta T + E_e \frac{h_n - z}{\kappa}} \qquad \text{Equation 1}$$

where t_e is the enamel thickness, t_s is the steel thickness, E_e is the Young's modulus of the enamel, E_s is the Young's modulus of the steel, $\Delta\alpha$ is the difference in the thermal expansion, ΔT is the amount of cooling from the onset of residual compressive stresses, and k is the radius of curvature and the term (h_n-z) is the distance from the neutral axis. From this, the stress distribution in a 2 layer system can be schematically shown as in Figure 1.

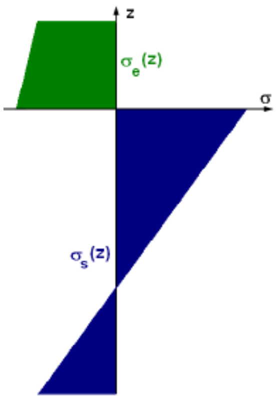


Figure 1. Tension and compression in the enamel-steel composite[8]

The Young's modulus of the enamel can be theoretically calculated in GPa using the Yamane and Sakaino approach in Equation *2*.

$$E = \frac{0.0093 * \rho}{M} * \sum \left(T_{m,i} * X_i \right) \qquad \text{Equation 2}$$

where ρ is density, M is the molar weight of the oxides, T_m is the melting point of each oxidic component of the frit, and X_i is the molar fraction of that oxide.[9] The frit density can be measured by the Archimedes Principle, and weighted averages of the frit chemistry oxide molar percentages are used. The elastic modulus is measured experimentally by a sonic resonance method.[10] Specifically, ASTM C1259 "Standard Test Method for Dynamic Young's modulus, Shear modulus, and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration" can be used. A singular elastic strike with an impulse tool creates a mechanical resonance within a test sample from which the modulus can be determined.

Estimation of the in-plane stresses in a single coat of enamel on a plane of steel is possible once the thermal expansion coefficients and elastic modulus are determined. In reality, geometries are more complex and multiple coats of enamel are used. Enameled steel ware often has a number of holes, slots, flanges, embosses, and other shapes.

Finite element analysis (FEA) is a powerful tool for determining the stress field in the enamel by mathematically solving large complex problems by breaking the geometry down into building blocks called finite elements. The applicable differential equations are thereby transformed into thousands of equations solvable by linear algebra. FEA predicts the performance of a design and is currently used in various branches of engineering and science such as mechanics, heat transfer, fluid dynamics, electromagnetism, acoustics, biomechanics, and more.[11, 12]

FEA models contain a geometry, materials, excitations, and constraints to calculate fields and potentials. The geometry is also called the domain or mesh and is broken down into elements. The traditional linear algebra equations are applied to elements at intersection points called nodes.[13] For porcelain enamels, the materials are the coatings and substrates while the excitation is the strain created by thermal expansion differences. The geometry would be the coated ware.

Procedure

The first step was to validate inputs for the FEA models experimentally to properly define boundary conditions and materials properties. Design of Experiment (DOE) studies to measure the torsion resistance of different ground coat/cover coat combinations were generated using the EChip software package. Overall, these were run using two different ground coats and four different cover coats with the coefficient of thermal expansion and firing conditions as input variables and determining the torsion angle via the PEI T-5 torsion test.

The materials selected for testing and modeling are shown in Table 1. Cover coats C and D were selected for the first DOE because they were novel coating materials developed by Ferro. The second set of cover coats (E and F) were selected because of their very similar chemistry and therefore the hypothesis that they should have similar moduli. The Young's modulus of steel is a literature value; for the enamels, it was calculated using the Yamane and Sakaino approach. The thermal expansion and glass temperature were measured using Orton push-rod dilatometry run on cast annealed bars of each enamel powder. The dilatometer bar of enamel A was machined down to dimensions suitable for experimental measurement of the elastic modulus via ASTM C1259.

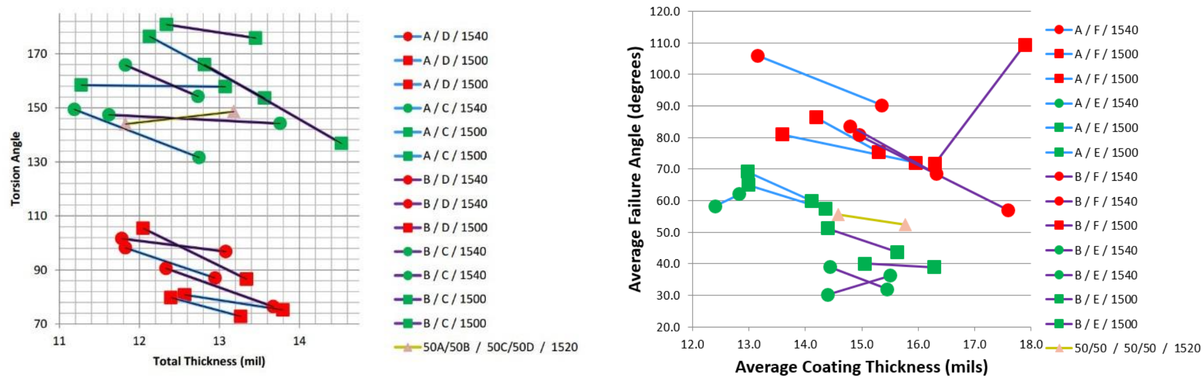
Material	**ρ (g/cc)**	**E (GPa)**	**α (x 10^{-6}/K)**	**T_g**
Steel	7.86	200	12.1	N/A
Ground Coat A (Base Coat)	2.70	66.0	10.4	833°F (445°C)
Ground Coat B (Pyrolytic)	2.62	60.5	8.9	907°F (486°C)
Cover Coat C (Water-Clean)	2.89	43.4	10.7	768°F (408°C)
Cover Coat D (Evolution®)	2.68	58.0	8.5	881°F (471°C)
Cover Coat E (Soft White)	2.69	56.9	10.7	824°F (440°C)
Cover Coat F (Hard White)	2.67	61.2	8.8	892°F (478°C)

Table 1. Material selection

The modeling procedure of the project was to simulate the residual stresses in the cover and ground coats using the FEA software package Lisa. The input values of Young's modulus, α, and density are those of the two ground coats and four cover coats tested in the two DOEs. A literature value of 0.21 was used for the Poisson ratio of steel. The first models were 2D with 1 coating and complexity was increased up to 3D models with both ground coat and cover coat as well as a center hole. The models are all under the assumptions that there is perfect adhesion between the coatings and the steel, there are no imperfections or impurities within the enamels, edges are sharp and not rounded, the enamel coatings are thin enough to ignore thermal gradients that may appear, the temperature drop on cooling was the same for each model, and any bending in the model is a result from displacements exaggerated in the X, Y, and Z directions. The layer ratios used were 0.75 steel, 0.15 ground coat, 0.15 cover coat out of 1.05

Results and Discussion

The results of the two DOE studies that tested the torsion angle of the ground and cover coat combinations are shown in Figure 2. The first DOE seemed to have contradicted the theory that a larger expansion coefficient increases the compressive thermal stress in the enamel to the steel. The second DOE repeated the experiment with the material selection altered slightly to reduce the influence of confounding variables. The result of the second DOE confirmed the theory that a larger expansion will increase the strength of the material when the elastic modulus is roughly the same between the two enamel cover coats. The materials properties were used as inputs for the FEA models.



(a) (b)

Figure 2. Results from the two DOE studies

Confirmation of the calculated elastic modulus was done by machining the expansion bar of enamel down to a size suitable for sonic modulus testing by ASTM C1259. The experimentally obtained moduli of 65.3 and 66.6 GPa closely agreed with the calculated value of 66.0 GPa.

Results are shown in Figure 3 for a modeled domain of a 2 x 1 rectangle approximating a lab 6" x 12" test plate.

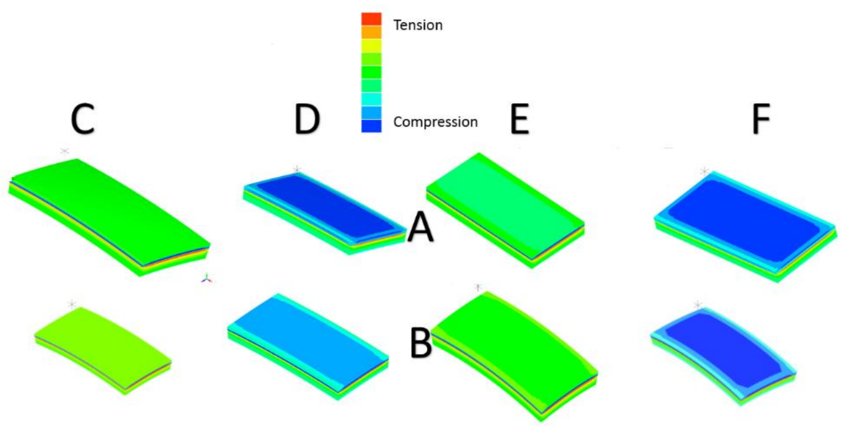
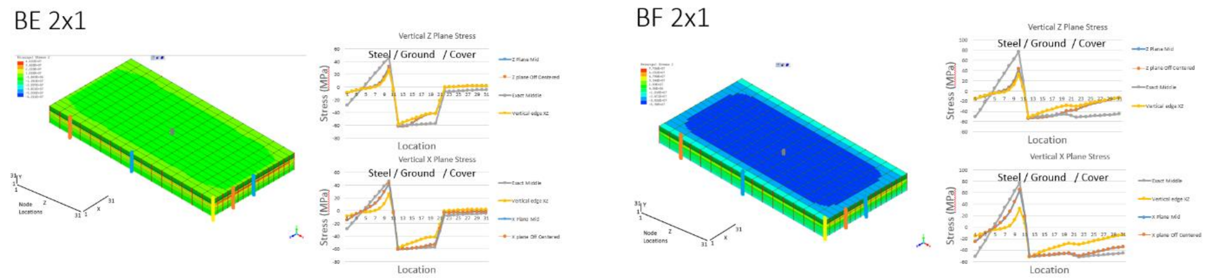


Figure 3. FEA models of 2x1 three-dimensional two-coat models

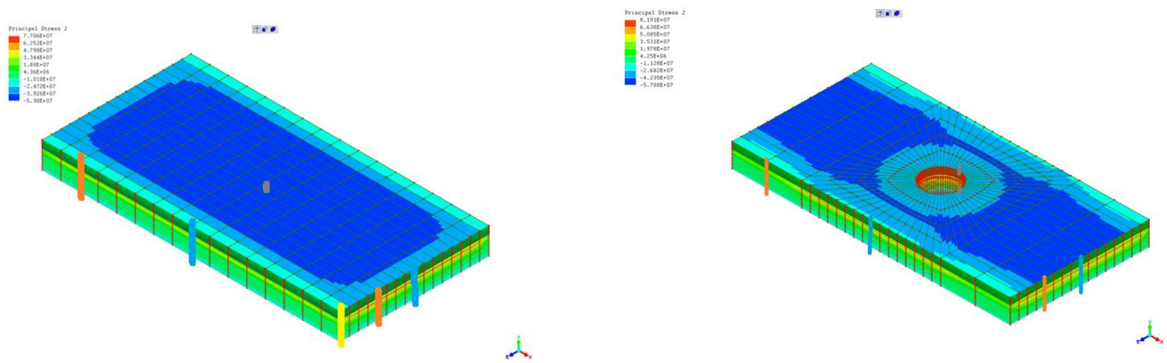
The compressive stress was determined by FEA for all the coating combinations and analyzed along the different locations along the y-axis cross-section at different points along the z-axis length and x-axis width of the domain. Combination BE, which had a lower residual cover coat stress, and BF, which had a higher residual cover coat stress, are shown in Figure 4 for comparison. The decrease in residual compression at edges correlates with the known greater susceptibility of enamel to edge chippage.



(a) (b)

Figure 4. Cross-sectional stress for (a) low stress combination BE and (b) high stress combination BF

A center hole was added to the domain to better simulate actual enameled ware that might contain a hole or slot for a fastener. The significant effect on the residual compressive stress field is shown in Figure 5.



(a) (b)

Figure 5. Side by side of the stress distribution for BF (a) without a hole and (b) with a center hole

The areas under the stress distribution curves were integrated to rank the coating combinations in the 2 x 1 models. The largest ground coat compressive stress is from the combination BC, and the largest cover coat compressive stress is from AF. When the two stress concentrations are totaled, coating BF had the largest overall and evenly distributed stresses in the cover and ground coats.

Conclusions

The two DOE studies showed the coating fracture resistance was directly influenced by thermal expansion differences as well as the interactions between the different Young's moduli. There was good experimental agreement in the theoretical Young's modulus calculations and the experimental value of ground coat A measured by ASTM C1259. This appears to be an accurate approximation of the Young's modulus for each glass suitable for FEA model inputs until more samples can be tested. The FEA model qualitatively reproduced the results of the torsion testing DOEs. Any combination with a harder ground coat or cover coat increased the residual compression for enamels with similar Young's modulus. The relative magnitudes of the stress distribution agreed with the two DOEs and prior literature. Some combinations had different locations for the maximum residual compressive stress. Reductions in compression at edges agreed with known experience. It was possible to drive geometry changes into the model such as a center hole. The models showed the cover coat areas around a hole are more fragile than a solid surface. The system with the highest overall stress was BF. While experimental results suggest a hard ground coat and a hard cover coat would have the highest resistance to strain or chippage, possible trade-offs could be weaker bond, strain lines, and less flow during firing. Future work would have the goals of completing comparison of experimentally measured Young's Moduli to the calculated values as well as scaling the model up to using CAD drawings of actual enameled parts to facilitate design and prototype work.

Acknowledgements

The following individuals are thanked for their support on this project:

- Dr. Mark De Guire at Case Western Reserve University, for serving as the senior project advisor for Brad Potter and Nick Carbo
- Kyla McKinley at Ferro for helping with coating and testing of torsion bars
- Eric Jelen for helping to make and test expansion bars
- Jonathan Salem at NASA-Glenn for running the sonic resonance testing of the expansion bar of ground coat A
- Renee Pershinsky for proofreading.

References

[1] Paul L. Smith, "Chipping Resistance of Enamels," *Proc. PEI Tech Forum* **3**, pp. 37-47 (1938).

[2] D.C. Bowman, "Stress as Related to Physical Properties of Titania Cover Coats," *Proc. PEI Tech Forum* **26**, pp. 237-244 (1964).

[3] Mitchell Horton and Andrew Stash, "Chip Resistance of Two-Coat/One-Fire Porcelain Enamels as Determined by Torsion Testing," *Proc. PEI Tech Forum* **56**, pp. 1-7 (1994).

[4] Joseph F. Uher and Charles M. Loane, Jr., "Effect of Rate of Temperature Change on Stress in Porcelain Enamel," *Proc. PEI Tech Forum* 41, pp. 173-7.

[5] William D. Faust, "Stress and Strain in Enamel Composites: A Practical Viewpoint," *Proc. PEI Tech Forum* **59**, pp. 101-111 (1997).

[6] Steven Cooreman, Philippe Gousselot, Marc Leveaux, Patrick Pol, Joachim Antonissen. "Understanding thermal wrapping and sagging in enameled steel parts through an integrated FE simulation" ArcelorMittal Global R&D Gent, 2009

[7] A.I. Andrews, Silvano Pagliuca, William D. Faust, *Porcelain (Vitreous) Enamels: The Preparation, Application and Properties of Enamels*, (The International Enamellers Institute: Mantova, Italy, 2011), pp.65-88.

[8] Filip Van den Abeele and Patrick Goes, "Multiphysics Approach to Model Solidification during Enamelling," *Excerpt from Proc. COMSOL Users Conference* (2007), p.1.

[9] Yamane, Masayuki, and Teruo Sakaino, "Calculation of Young's Modulus of Glass from its Chemical Composition and Density," *Glass Technology*, **15**, 5, October 1974.

[10] R.E. Cowan, A.W. Allen, and A.L. Freidberg, "Effect of Temperature on Modulus of Elasticity of Porcelain Enameled Steel," *J. Am. Ceram. Soc.*, **39**, 9, September 1956.

[11] John R. Brauer, Ed., *What Every Engineer Should Know About Finite Element Analysis, Second Edition, Revised and Expanded*, (Marcel Dekker: New York, 1993), pp. 1-7.

[12] Barna Szabó and Ivo Babuška, *Introduction to Finite Element Analysis*, (Wiley: Chichester, UK, 2011), pp. 1-14.

[13] Tom Wormald, "Finite Element Analysis Applications for the Appliance Industry: Solutions in Steel™," *Proc. PEI Tech Forum* **63**, pp. 75-80 (2001).