



Modeling of Vitreous Porcelain Enamel Mechanical Properties

Charles Baldwin (R & D Manager, Ferro Corp)
May 26, 2015

Introduction

- Porcelain enamels are selected for use as protective coatings for their heat resistance, hardness, and abrasion resistance but are brittle
- New developments are driving a need to better quantify and optimize the enamel fracture resistance
 - Usage of thinner gauge steel
 - Adoption of water-cleaning cover coats on oven cavities
 - New color pyrolytic enamels



Crazing
on oven
panel



Spalling

Residual Compressive Stress

- Enamel is a bilayer composite of metal and glass with the strength coming from being in a state of residual compression that develops on cooling
- Compressive stresses are caused by a mismatch of thermal expansion
- Stress in the enamel can be theoretically calculated by

$$\sigma_e = \frac{E_e (\alpha_e - \alpha_s) (\Delta T)}{\frac{t_e}{t_s} \frac{E_e}{E_s} + 1}$$

- Stress σ varies with thickness t , Young's modulus E , CTE mismatch $\Delta\alpha$, and temperature drop during cooling ΔT

Project Description

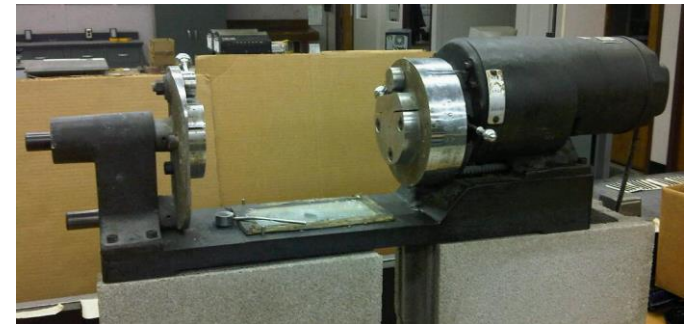
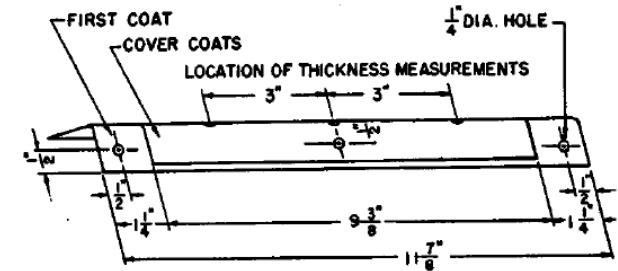
- There is ongoing sponsorship of senior research projects at Case Western Reserve University by the Ferro Corporation
- The residual stress states of cover and ground coat combinations were modeled with FEA (Finite Element Analysis)
 - FEA is a numerical technique for finding approximate solutions to boundary value problems for differential equations
 - Define a mesh geometry, materials properties, apply a gradient, and software calculates the result
- Compared the models with theoretical and experimental results
- Allowed the validity of standard models to be assessed to optimize the enamel durability

Goals

- Model the stress states in combinations of hard and soft ground coats and cover coats for quantitative understanding
- Compare models with and without added geometries
 - PEI 101 design guidelines
 - Parts that will be enameled
- Have models for reference when comparing to experimental results

Previous Work

- The PEI T-5 torsion test was used to study the strain resistance of different ground coat/cover coat combinations
- One end of the sample is fixed and the other is rotated at 100 degrees per minute
- Failure identified by visual inspection
- Test stopped when spalling begins
- Angle to failure is measured



Material Selection

Steel

α (/°C)
$12.1 * 10^{-6}$

Ground
Coat

Enamel	α (/°C)	T_g (°C)
A	$10.4 * 10^{-6}$	445
B	$8.9 * 10^{-6}$	486

Original
Cover Coats

Enamel	α (/°C)	T_g (°C)
C	$10.7 * 10^{-6}$	408
D	$8.5 * 10^{-6}$	471

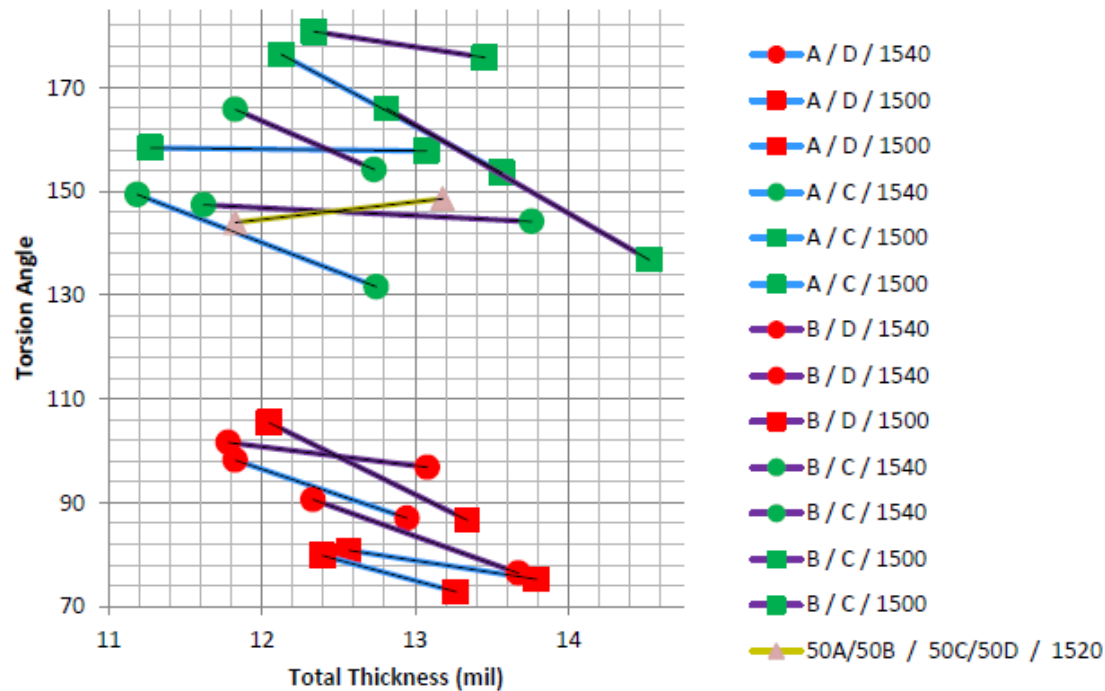
C – AquaRealEase®; D – Evolution®

Titanium
White
Cover Coats

Enamel	α (/°C)	T_g (°F)
E	$10.7 * 10^{-6}$	440
F	$8.8 * 10^{-6}$	477

Expectation: low $\alpha \rightarrow$ large compressive stress, stronger coatings

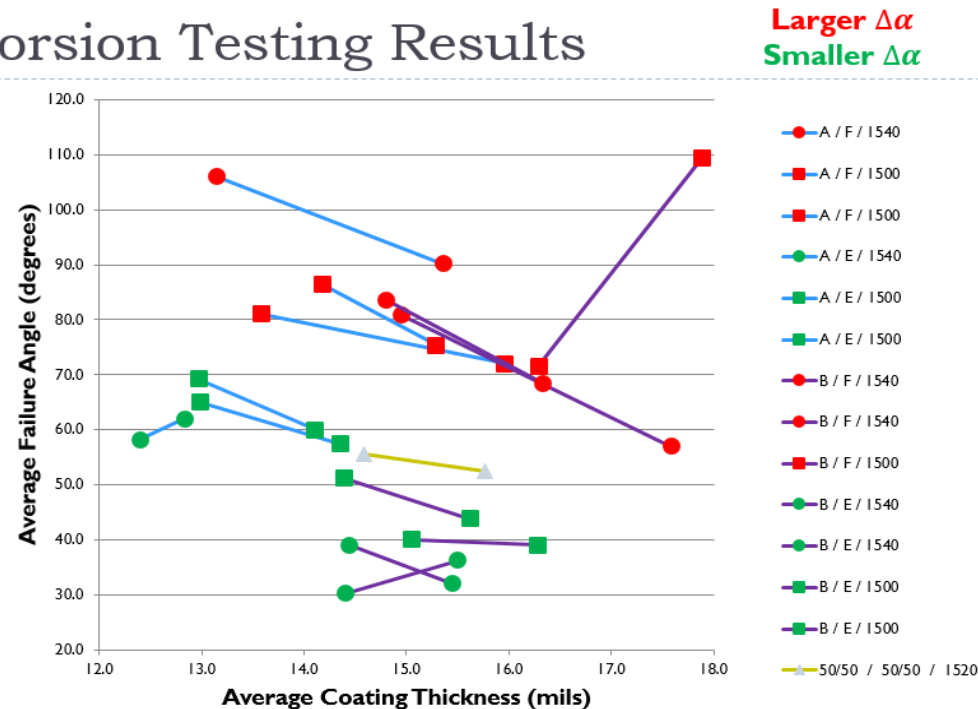
First DOE Result



- A larger difference in enamel and steel expansion did not increase enamel strain resistance
- Suggested different chemistries played a role by changing the Young's Modulus

Second DOE Result

Torsion Testing Results



- Ran with soft and hard white titanium cover coats to reduce the influence of confounding variables
- A larger CTE difference had a higher torsion angle

Young's Modulus Calculation and Measurement

- Theoretical calculations with Yamane and Sakaino approach

$$E = \frac{0.0093 * \rho}{M} * \sum (T_{m,i} * X_i)$$

- E = GPa ρ = g/cc M = g/mol T = K X = mol/mol
 - Measured density using Archimedes Principle
 - Used weighted averages of frit chemistry oxide molar percentages
- Measured with ASTM C1259 “Standard Test Method for Dynamic Young’s Modulus, Shear Modulus, and Poisson’s Ratio for Advanced Ceramics by Impulse Excitation of Vibration”
 - A singular elastic strike with an impulse tool creates a mechanical resonance within a test sample from which the modulus can be determined

CTE Bars

- Frit for cover coats E and F were mixed and milled
- 6 CTE bars were made from the 2 ground coats A and B as well as the 4 cover coats C, D, E, and F
- Expansion measurements were run on each bar
- Began machining the bars for sonic measurement testing at NASA Glenn for Young's modulus with ASTM C1259



CTE bar D compared for size to machined bar A

Model Inputs

	Sample	CTE (x 10 ⁻⁶ /°C)	Calculated Young's Modulus (GPa)	Young's Modulus Experimental (GPa)	Tg (°C)	Density (g/cc)
Soft ground coat	A	10.4	66.0	66.0	445	2.70
Hard ground coat	B	8.9	60.5		486	2.62
AquaRealEase®	C	10.7	43.4		408	2.89
Stainless Evolution®	D	8.5	58.0		471	2.68
Soft white cover coat	E	10.7	56.9		440	2.69
Hard white cover coat	F	8.8	61.2		477	2.67
				Poisson's ratio		
Steel		12.1		0.23		

- A larger difference in CTE between enamels should lead to a higher compressive stress in the coatings
- A larger Young's Modulus should increase the compressive stresses

$$\sigma = E * \Delta\alpha * \Delta T$$

- Cooling considered from 768°F (409°C) to 77°F (25°C)

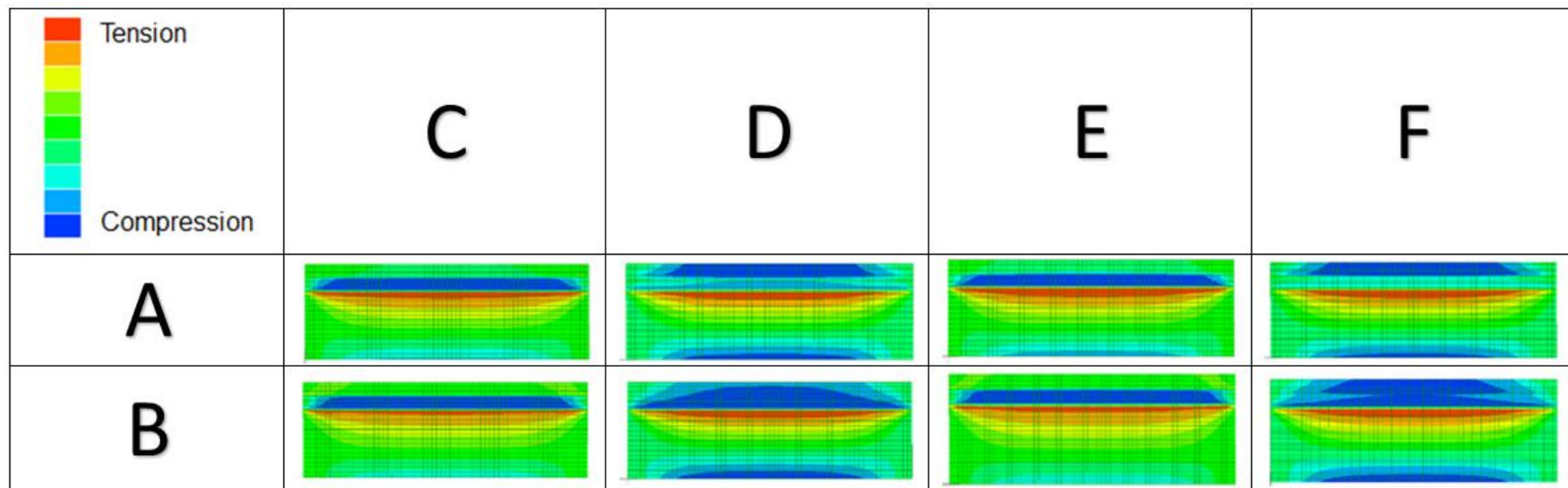
Lab Procedure

- Step by step process modeling using commercially available software
 - Begin with 2D 1 coat
 - 2D 2 coatings
 - 3D square 1 coating
 - 3D square 2 coatings
 - 3D rectangle 1 coating
 - 3D rectangle 2 coatings
 - 3D rectangle with hole 2 coatings – compare to PEI 101 design recommendations
- At each step evaluated whether the models agreed with existing theory and experimental results

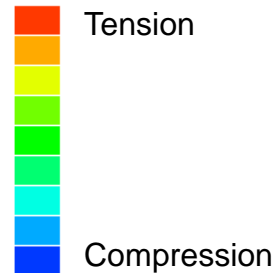
Modeling Assumptions and Inputs

- Perfect adhesion
- No imperfections or bubbles in the glasses
- Sharp edges
- Coatings are thin to ignore thermal gradients
- Each model had the same temperature drop
- All layer ratios were the same
- All layer interfaces were at the same nodes on all of the models

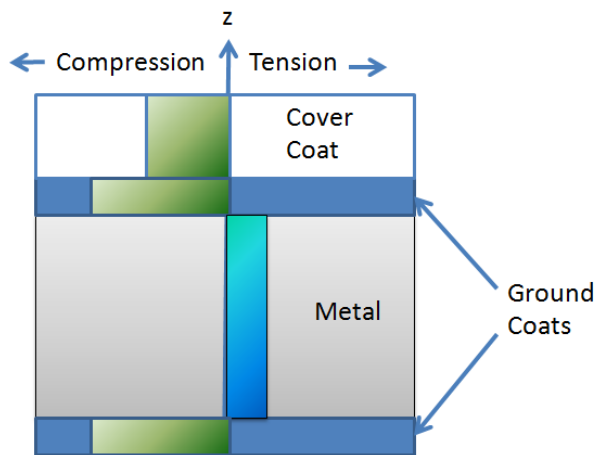
2D Models



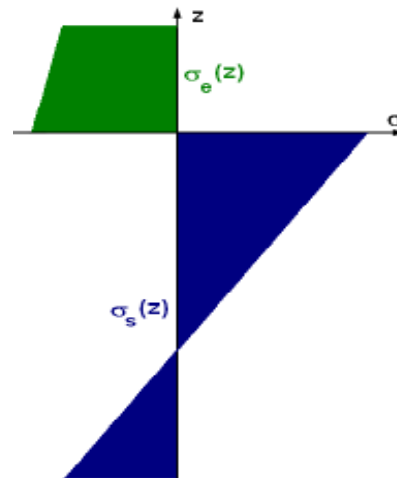
2D Model Vs Literature Data



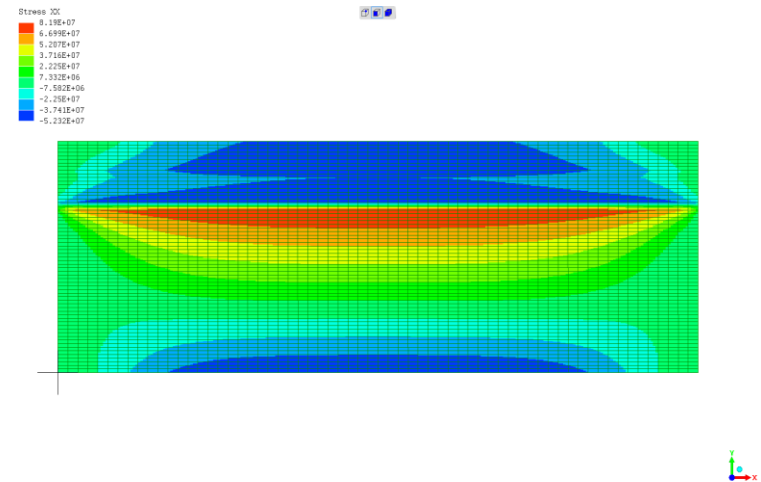
Paul Smith – Cover Coat



Abeele and Goes – Ground Coat

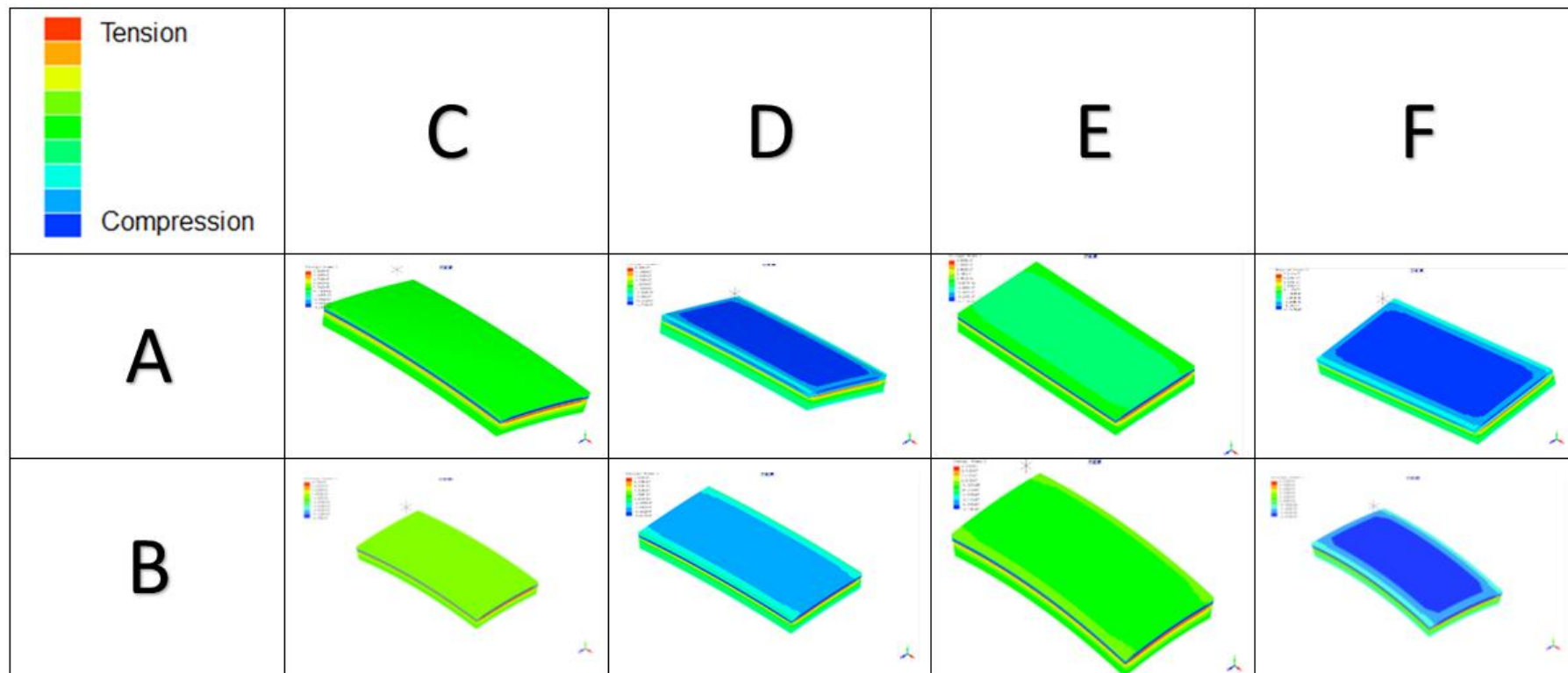


BF 2D FEA model

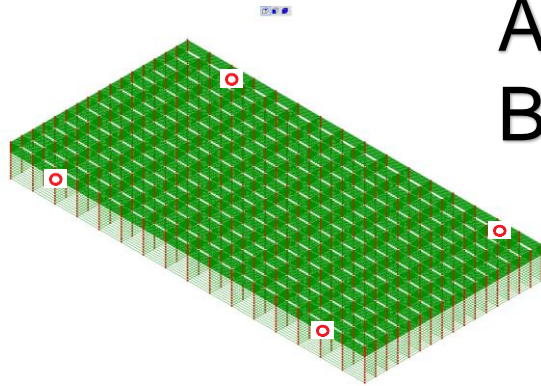


- 2D model result comparable to theory
- Extended to 2 x 1 rectangles approximating lab 6" x 12" (15 cm x 30 cm) test plates

2x1 Models 3D

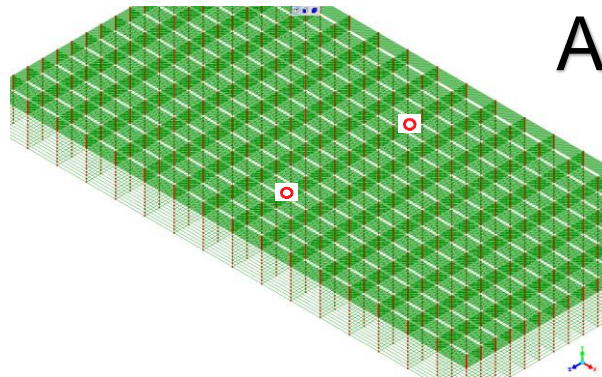


Highest Stress Locations

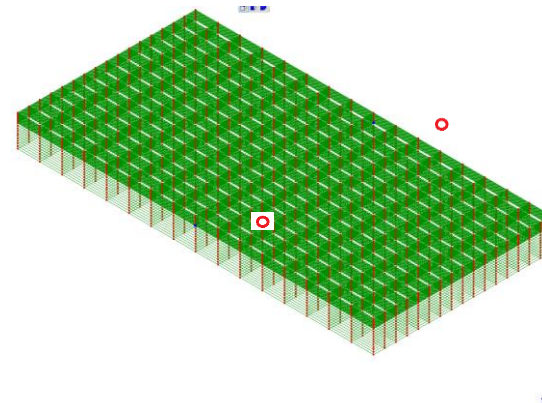


AC,AE,
BC,BE

- Maximum compressive stress is in different locations depending on the coating combination
- With AC, AE, BC, BE there are 4 locations each in the ground coat layer above the steel on the Z plane edge
- With AD and AF there are 2 locations each in the cover coat right above the ground coat
- For BD and BF there are 2 locations each in the ground coat just above the steel



AD,AF

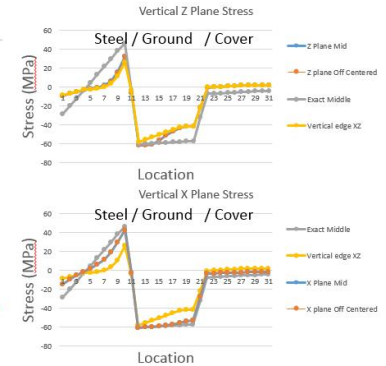
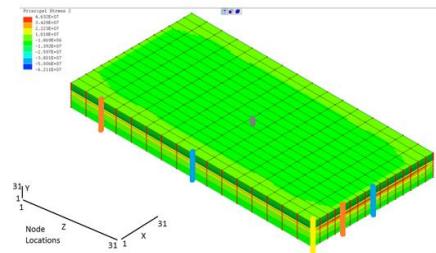


BD,BF

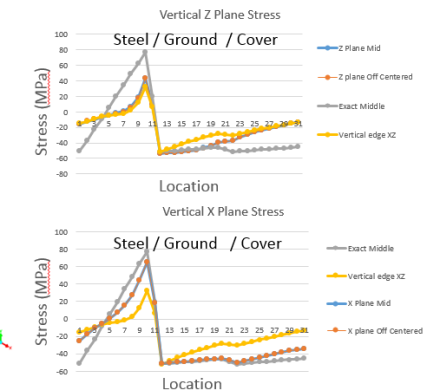
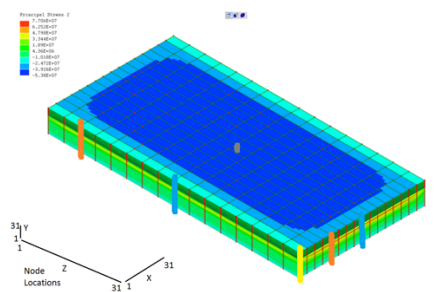
FEA

- Compressive stresses determined in 3 dimensions: x (width), y (cross-section), z (length)
- BE, which had a low stress, is compared to BF, which had a high stress
- The decrease in stress near edges on BF correlates with the known susceptibility of enamel to edge chippage, particularly sharp edges

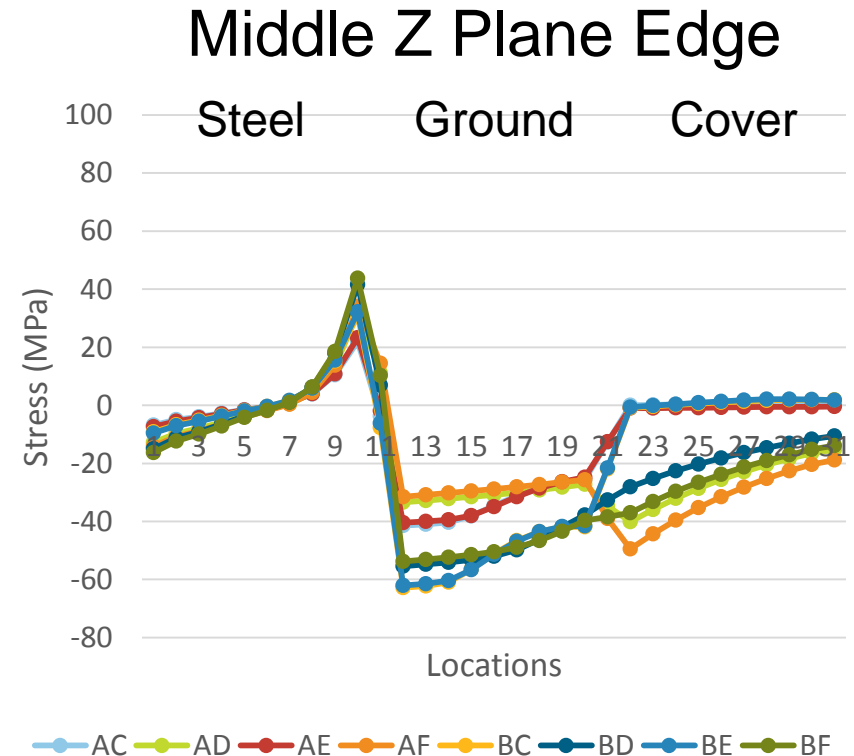
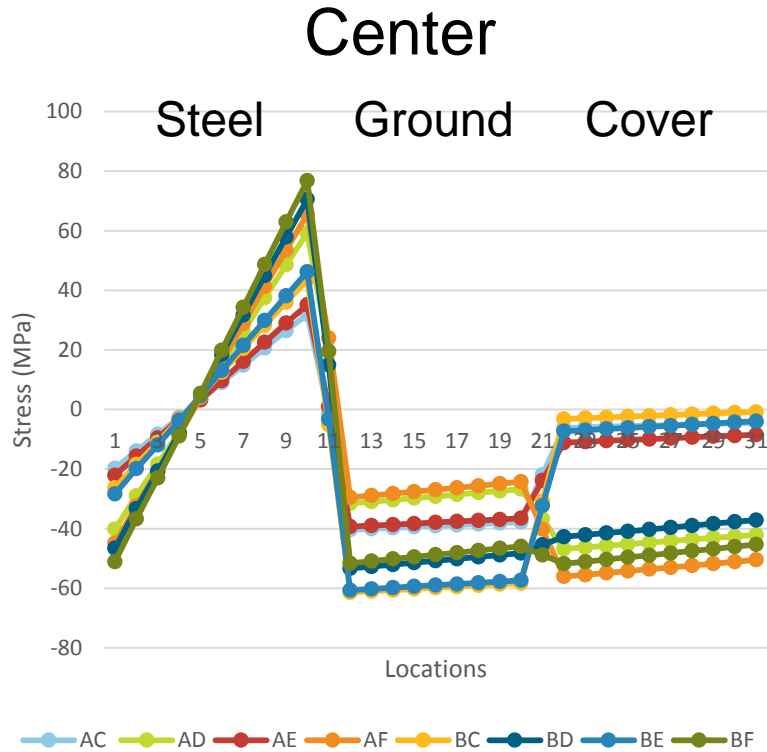
BE 2x1



BF 2x1

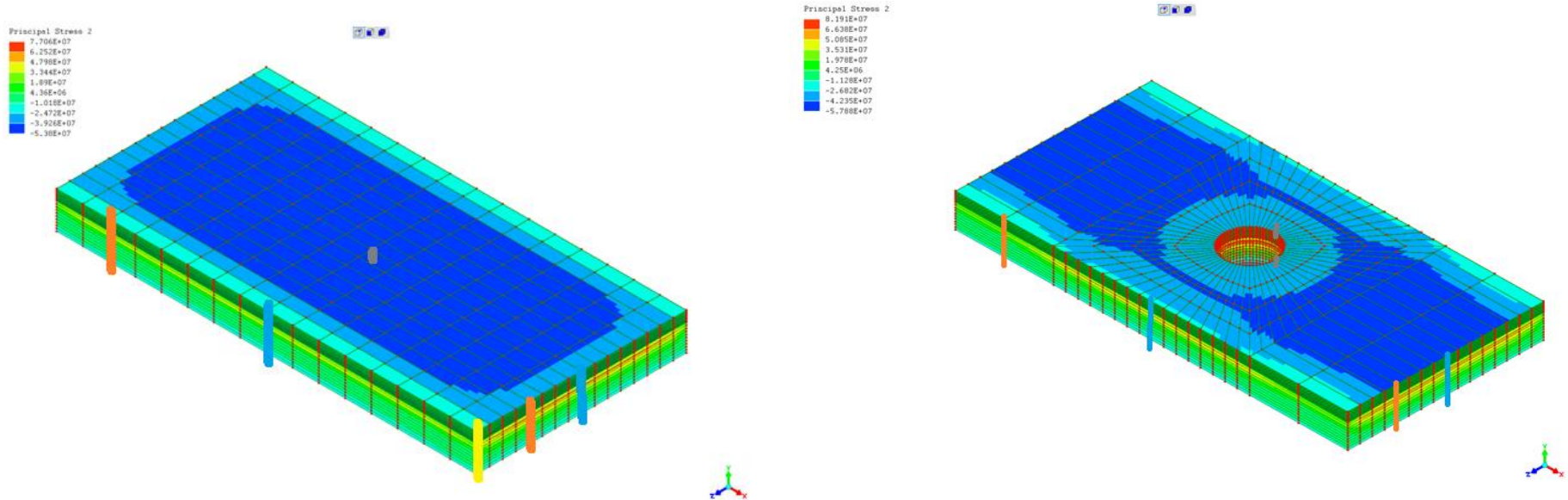


Center vs Edge Stresses 2x1 Models



- Stresses decreased at the edges for all combinations

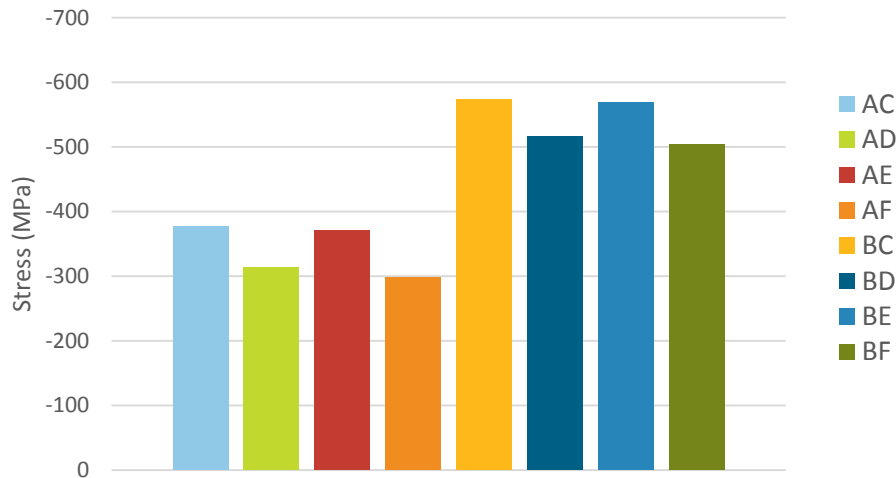
Center Hole



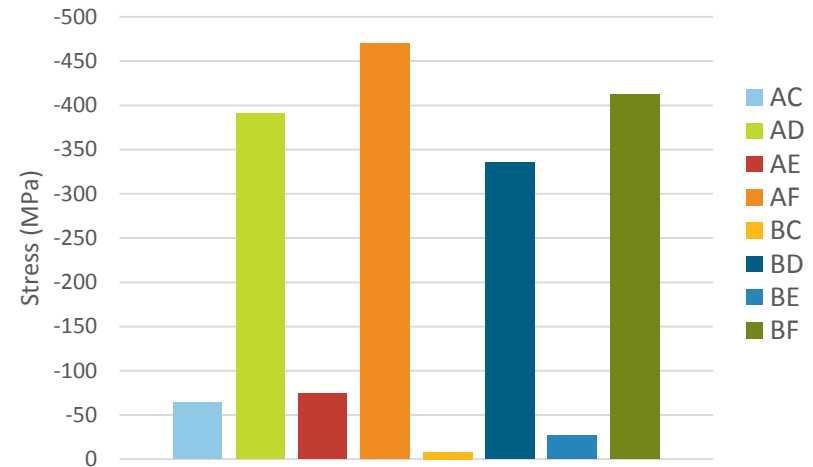
- Addition of a center hole reduced the maximum stress near the hole and at the edges

Area Under Curve for 2x1 Center Stresses

Ground Coat Stress Totals

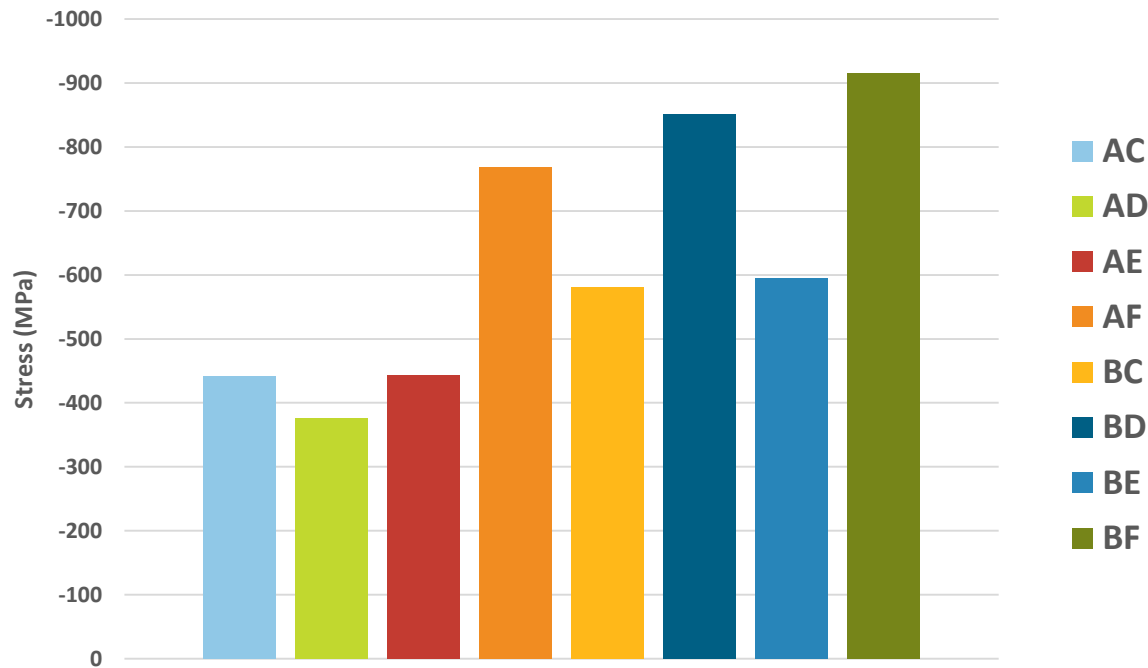


Cover Coat Stress Totals



- Areas under the curves were used to compare the total stress in the 8 ground coat/cover coat combinations in the 2 x 1 3D model

Total Enamel Stress



- Combination of hard ground coat B and hard ground coat F had the greatest residual compressive stress

Conclusions

■ Modeling

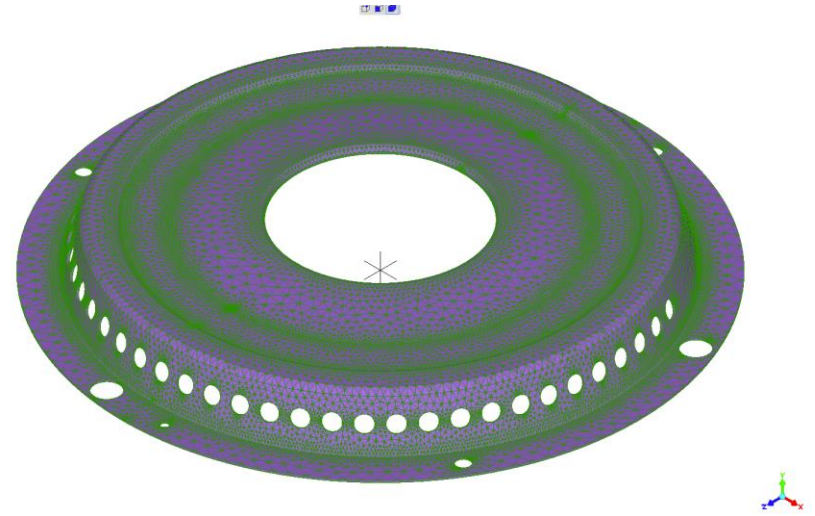
- There was good agreement in theoretical and experimental Young's Modulus measured via ASTM C1259
- Stress distribution agreed with prior literature and was able to quantify the stress through a sample
- Some combinations had different locations for their maximum compressive stresses; reduced compression at edges agreed with experience
- Was able to drive geometry changes such as holes into the model

■ Enamels

- Any combination with a harder ground coat or cover coat increased the residual compression
- Highest overall totaled stress is BF
- Trade-offs could be bond, strain lines, less flow during firing
- Coating strength is influenced by
 - $\Delta\alpha \rightarrow$ direct relationship
 - $E \rightarrow$ direct relationship

Future Work

- Machining of CTE bars for experimental confirmation of modulus data
 - Sonic resonance testing
- Investigation of strain resistance at edges experimentally
- Final goal to expand the simulations to a more in-depth geometry
 - Expanding to a coating using a CAD file of a part that is enameled



Acknowledgements

- Thank you to Whirlpool for providing steel for torsion bars
- 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