STRESS REDUCTION IN PORCELAIN STEEL SYSTEMS

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The question most often asked of porcelain enamel technical personnel is, "What can be done to reduce chipping, minimize crazing, lower warping, and eliminate spalling on enamelled parts processed in various segments of the industry?"

In many instances, these problems occur after final assembly, and, therefore, the remedies are usually very time consuming and costly. For various manufacturing processes, the residual stress of the enamel-steel system is an important factor in determining the success of the enamelling operation.
Additionally, with the movement to thinner-gauge steels, the amount of residual stress after firing will also be a critical design factor for the enamel glass system.

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Enamel systems are formulated to yield compressive stresses at the glass/steel interface at room temperature.
This is accomplished by designing the individual enamel to produce a lower coefficient of expansion than the base steel at room temperature.
For example, the enamel frit in Figure I has a lower coefficient of expansion than the steel, but as the enamel reaches its glass transition point, the enamel expansion becomes higher than the steel.
Initially upon cooling, the enamel is in tension. As cooling continues to room temperature, the enamel proceeds through the glass transition point into compression because of the lower coefficient of expansion.
The amount of this compressive stress value is directly dependent on the enamel's composition and its application to the steel substrate.

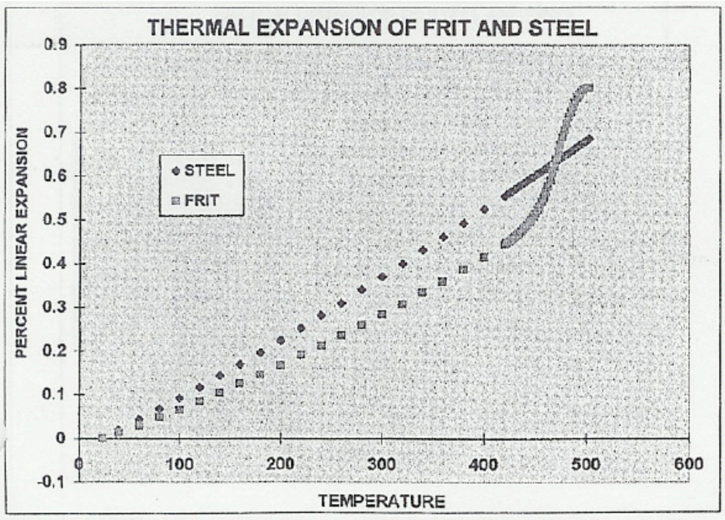

Figure 1. Thermal expansion of frit and steel.

The relative stress of an enamel-steel system is depicted in Figure 2, starting from room temperature with absolutely no strain (stress), to a set firing temperature in the furnace. Upon cooling, the enamel passes through an area of tension as the temperature is decreased. Ultimately, this becomes the residual stress at room temperature.

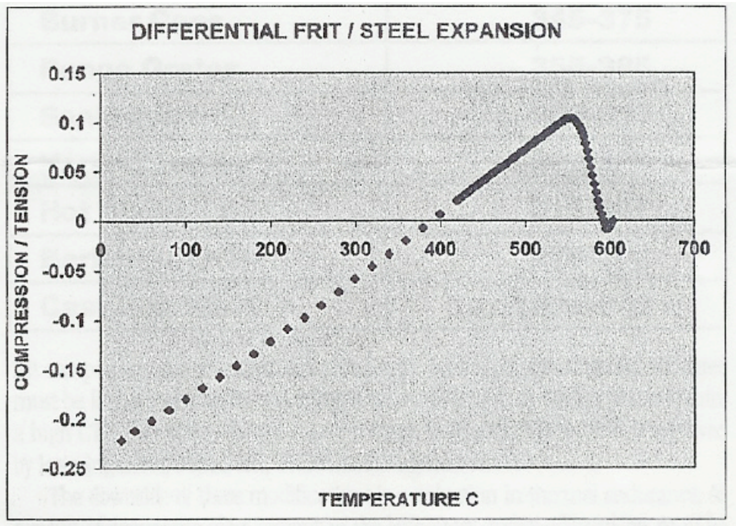

Figure 2. Difference in expansion coating in compression after firing.

Enamel frits are designed to be in compression, but the amount of stress depends on the enamelled part and its final working environment. One enamelled piece may require thermal durability, while another may require thermal shock resistance.

In the first example, the pyrolytic-type enamel would be designed with a lower thermal expansion, which, in turn, would yield a higher stress and excellent craze resistance. As oven steel expands due to the high temperature (approximately 900°F /482°C) needed during the cleaning cycle, the enamel must also expand with the steel substrate. If the enamel does not remain in compression, crazing/spalling will occur as a defect.
In the latter case for burner grates, a high thermal expansion would result in better thermal shock resistance with lower stress. In both cases, the systems would possess compressive stresses, but the differences in compression between the two enamels will affect other enamel glass properties.

Glasses need compressive stress to promote strength and adhesion. However, an enamel with too high stress may be subject to warping and chipping; too low stress may be subject to crazing.
A balance must be maintained with all of the required physical and chemical properties to meet the manufacturer's specifications for the enamelled piece.

The stress in glass can be measured by several methods. One is by the warping test, which measures the amount of curvature/deflection of an enamelled test panel[1]. Another method is the loaded beam test, which directly measures the amount of weight necessary to neutralize the warp of a one-sided, enamelled strip. Residual stress in this test piece can be calculated through a mathematical formula. Steel preparation of the sample strips is very influential on the final stress result[2].

Another method that measures the stress in glasses is the coefficient of thermal expansion (CTE). By this method, it has been found that the measurement of a glass's CTE is very reproducible and accurate. The CTE can also determine the glass transition temperature and melting point. An automated Orton Dilatometer for CTE measurement has continually been utilized for screening and final development of many complex

enamel systems. It has been the tool of choice for measuring and modifying stress levels.
Individual oxide compositions (e. g., SiO_2, B_2O_3) , of multi-glass component systems are fundamental in the stress development, and, subsequently, inherent in the coefficient of thermal expansion (CTE).

Figure 3 shows a table of cubic (volume) expansion factors for various oxides. As can be seen, glass compositions high in silica, boria, alumina, and zirconia contribute significantly in lowering the CTE, while high alkali additions (Li_2O, Na_2O, K_2O) will increase the CTE.

Figure 3 – Cubic expansion factors for typical oxides in frit compositions [3]

SiO_2	5 to 38	MnO	105
TiO_2	30 to 15	FeO	55
$Zr\ O_2$	-60	CoO	50
$Sn\ O_2$	-45	NiO	50
$Al_2\ O_3$	-30	CuO	30
B_2O_3	0 to -50	Li_2O	270
Sb_2O_3	75	Na_2O	395
MgO	60	K_2O	465
CaO	130	CaF_2	180
SrO	160	Na_2SiF6	340
BaO	200	P_2O_5	140
ZnO	50		

At best, the selection of the various oxides in a glass composition will be a compromise for meeting the required chemical and physical properties. For example, black range grate enamels are formulated to yield the highest CTE without crazing, but still remain in compression to prevent spalling in a thermal shock environment. This is normally accomplished by higher amounts of alkali in the glasses. However, increased
amounts of alkalis are not conducive to good thermal durability properties for minimizing metallization or discoloration of the grate fingers. Other properties such as adherence (bond), basic colour, colour stability, and acid resistance must also be balanced for the enamel's total performance. Therefore, the final composition is a mixture of oxides that best fulfils the enamel's requirements, including CTE (stress).
A table of typical cubic CTE ranges for presently designed enamel systems is shown in Figure 4. These numbers may be applied either to wet or electrostatic powder systems. These are not absolute values, but, rather, a possible working range. There is a wide difference in CTE values, depending on the substrate and corresponding enamel system. Enamel systems ideal for a specific application will not perform universally.
Enamel systems must be tailored for various plant application processes, furnaces, part designs, and final end use.

Figure 4 – CTE value for Various enamel system	
Enamel coating	**Typical CTE ($X 10^{-7}$/in/in/°C)[4]**
Pyrolytic Range	255-285
Range Tops	290-320
Burner Caps	345-375
Range Grates	355-385
Sanitaryware	280-310
Range Tops	290-320
Hot Water Tank	315-345
Barbecue grills	270-300
Cast Iron white	320-335

Various curves are shown in Figure 5 for typical low-, medium-, and high-stress glasses versus steel.
Balancing the various oxides in a glass composition will yield the optimum composition for physical and chemical properties.

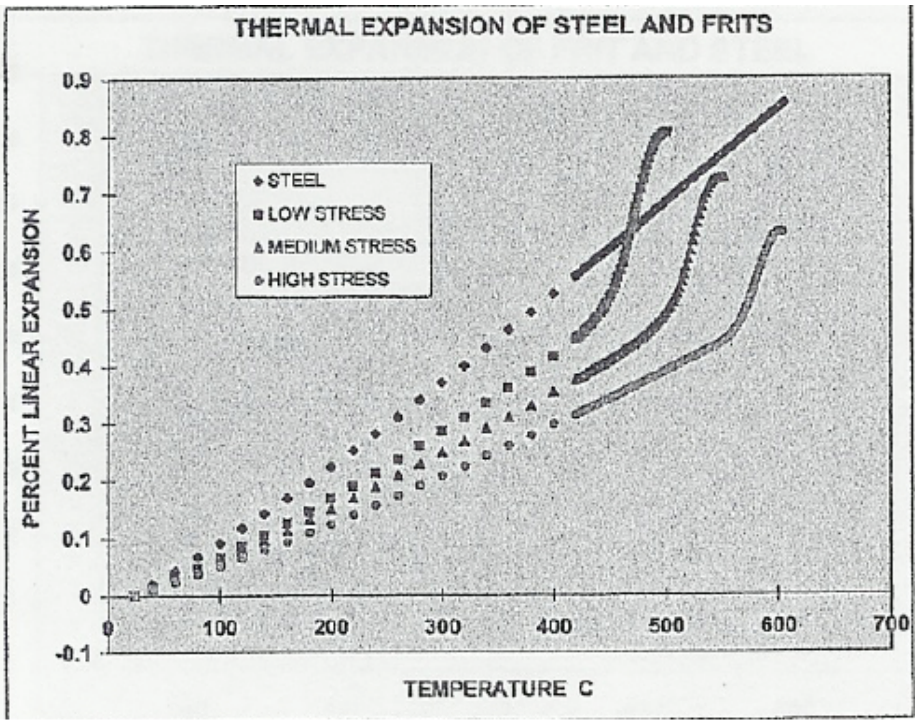

Figure 5. Coefficient of thermal expansion of high, medium and low stress Frits and steel

Ideally, stress reduction should be achieved through a combination of enamel frit composition design, fabricated part design, and application method. All three must be linked together for a successful enamelling process.
Range grates require a high CTE (low stress) for the thermal shock resistance.
Higher CTE is achieved by lowering silica, borax, etc., while increasing total alkali.

The downside of these modifications is a reduction in thermal endurance. As a result of developing glass systems in the laboratory, many adjustments must be made to comply with customer specifications and end-product requirements. Consistently high quality of the enamelled piece is the customer's ultimate goal.

While the advent of clean-only steel (e.g., no pickle or blasting) and special grades of thinner steel have made achievement of acceptable bond more difficult, it is imperative that a balance is maintained among thermal shock resistance, thermal durability, colour, and chemical properties. These same design factors are universally acceptable in developing enamel systems for self-clean oven cavities that require high stress and range tops that require medium stress.

Glass systems are continually developed to optimize individual properties, including stress reduction. This will ultimately benefit the enamelling process. *This is from a paper presented at the 60th Annual* Porcelain Enamel Institute (PEI) Technical Forum Back-to-Basics Workshop and Suppliers' Mart, May 11-14, 1998, Nashville,TN. ,

References

[1] PEI, Inc., Technical Manuals, T-3 Test for Warpage of Flatware.
[2] PEI, Inc., Technical Manuals, T-3D Loackd Beam Metbodfor Determination of Compressive Stress of Porcelain Enamel.
[3] Technology of Enamels, Professor V.V. Vargin.
[4](Linear CTE (α) = Cubic CTE (α^3) /3 = x 10-7/in/in/1°C)