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Evaluation method for the adhesion strength of vitreous enamel

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A new quantitative evaluation method and the formula for vitreous enamel were proposed. The three-point bending strength was measured by loading on the superposition of test piece which sandwiched glass layer partly between two steel sheets. The adhesion strength (σ) was calculated using the following equation, $\sigma = 3PLh/2b \cdot Eg/\{Egh^3 + Es(h'^3 - h^3)\}w$ here, P; bending strength, L; length of span, b; width of glass layer, Eg; Young's modulus of glass, Es; Young's modulus of steel, h; thickness of glass layer, h′; thickness of superposition of test piece. The evaluation method for vitreous enamel of this experiment agreed with the empirical evaluation and may be applied to an actual situation.

The typical evaluation methods of the adhesion strength of vitreous enamel include the steel ball drop test [1, 2], the press test [3] and the PEI methods [4–6]. These methods are not quantitative evaluation methods.

The steel ball drop test is carried out as follows: the test piece of vitreous enamel is horizontally fixed to the tester with the glass face upwards; a steel ball 36.51 mm in diameter with a mass of approximately 200 g is dropped by gravity from a height of 45 cm and the peeling of the glass layer is visually checked.

The press test, using an apparatus consisting of a die and a punch, as illustrated in Fig. 1, is carried out as follows: the test piece is pressed with the punch of a hand press to break the glass layer by permanent concave deformation, and visual checking is done for the glass still remaining on the concavely deformed surface. The more the glass that remains, the better the adhesion is. This method is, therefore, an in-place evaluation method.

The PEI method is carried out by bringing a bundle of 169 conductive metallic needles into contact with the test piece which is permanently concavely deformed by the hand press in the same way as in the press method, and checking for remaining glass area by measuring the numbers of live and dead needles. The adhesion strength is calculated using:

$$\text{Adhesion}(\%) = \{(169 - \text{number of live needles})/169\} \times 100.$$

Although this method is the only numerical one among the three methods, it is no more than an index system that uses a special apparatus instead of a visual check. The press and the PEI methods are inaccurate because pressure-welded glass sometimes remains in the center of the permanently concavely deformed test piece.

We present the development of a test method in which an apparatus for determining three-point failure in bonding is applied to a test piece prepared by sandwiching a glass layer between two steel sheets. The adhesion strength of vitreous enamel to glass corresponds to the maximum mechanical failing load, so the adhesion strength of vitreous enamel can be determined. The formula for calculating the adhesion strength in this method is introduced and the method is validated experimentally.

In the experiment, alkali boronsilicate ground coat frit was used to coat the steel sheets. Its composition and main physical properties are listed in Table I. The test piece was prepared using a steel sheet 5 mm wide, 50 mm long and 1.5 mm thick. The rectangular steel sheets are degreased and masked except over a length of 11 mm from the edge, and coated by spraying the ground coat slip so as to make the calcined glass layer 0.2 to 0.4 mm thick. After drying them, the coat surfaces of two steel sheets are put together. Sets of the two steel sheets are placed horizontally and calcined at 700, 750, 800, 850, and 900 °C, respectively, for 10 minutes in an electric furnace. The schema of the calcined test piece used for quantitative evaluation is illustrated in Fig. 2.

The quantitative evaluation test was carried out by placing a test piece horizontally, and applying a load to the center of the superposed part at a speed of 10 mm/min, with the three-point bending strength tester as illustrated in Fig. 3, to break the glass.

First, the adhesion strength of the ground coat frit for glass-coated steel used in the experiment was determined by the press test. The steel sheets were degreased and coated by spraying the ground coat frit so as to make the calcined glass layer approximately 0.3 mm thick. The steel sheets were calcined at 700, 750, 800,

TABLE I Composition and fundamental physical characteristic of the ground coat frit

Oxide	mol %
SiO_2	51.0
TiO_2	3.5
ZrO_2	0.5
Na_2O	17.0
K_2O	0.5
Li_2O	2.5
CaO	2.6
BaO	4.4
B_2O_3	12.5
Al_2O_3	3.0
CoO	1.5
NiO	1.0
Coefficient of expansion	$103 \times 10^{-7}\,^{\circ}C^{-1}$
softening point	430 °C

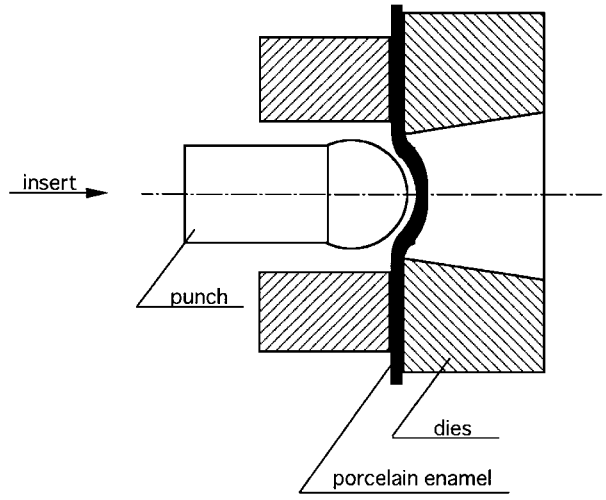

Figure 1 Assembly for measuring the adherence of porcelain enamel.

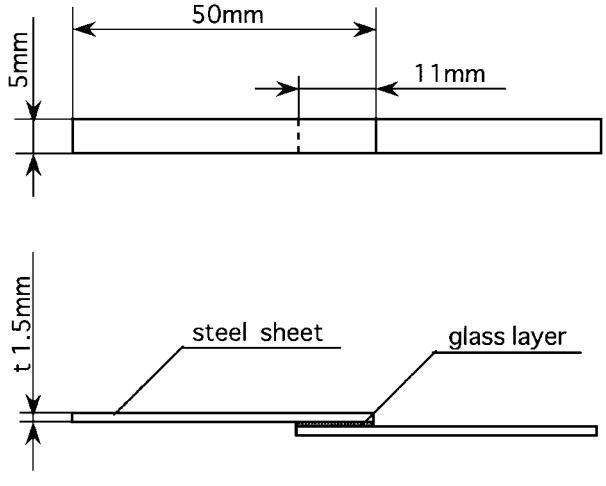

Figure 2 Schema of the test piece.

850, and 900 °C, respectively, for 10 minutes. The press test results of the test pieces are illustrated in Fig. 4. It can be seen that the relationship between the calcining temperature of the ground coat frit and the adhesion strength was as follows: adhesion strength of the test piece calcined at 700 to 750 °C was poor since little glass remains on the concave surface; that of the test piece calcined at 800 to 850 °C was good since more glass was observed there; and that of the test piece calcined at 900 °C was slightly lower than that of the test piece calcined at 800 to 850 °C.

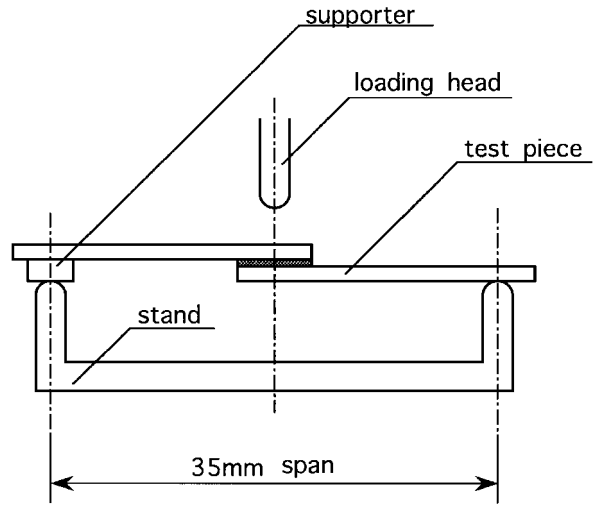

Figure 3 Measurement schema of adhesion to employ three-point bending strength.

The superposed part in the test piece used in the quantitative evaluation was comprised of glass and steel sheets. The bending stress, σ (Mpa), of such a test piece prepared by combining two or more materials is determined by the following general formula [7]:

$$\sigma j = \frac{M \cdot Ej \cdot ej}{\sum_{i=1}^{n} (Ei \cdot Ii)} \tag{1}$$

where M = bending moment (Nm), I = moment of inertia of area (m^4), ej = distance between the neutral surface of the superposed surface and the adhered surface (m) and E = Young's modulus (Mpa).

The determination methods of M, I and ej will be described below.

The bending moment, M, is the product of the load and the distance of the arm. The bending moment, M, therefore will be

$$M = \frac{P \cdot L}{4} \tag{2}$$

The moment of inertia of area, I, depends upon the shapes of the rotating shaft and the object. The moment of inertia of area is determined by assuming an η-axis through the center, O, of the superposition as illustrated in Fig. 5, and integrating the whole area of the superposition. Since the superposition comprises the glass layer and the superposition of the steel, each moment of inertia of area is determined in this way.

The moment of inertia of area of the glass layer, Ig, is expressed by:

$$\begin{aligned} Ig &= \int_{-h/2}^{h/2} \eta^2 \, dA \\ &= \int_{-h/2}^{h/2} \eta^2 \, b d\eta \\ &= \frac{b \cdot h^3}{12} \end{aligned} \tag{3}$$

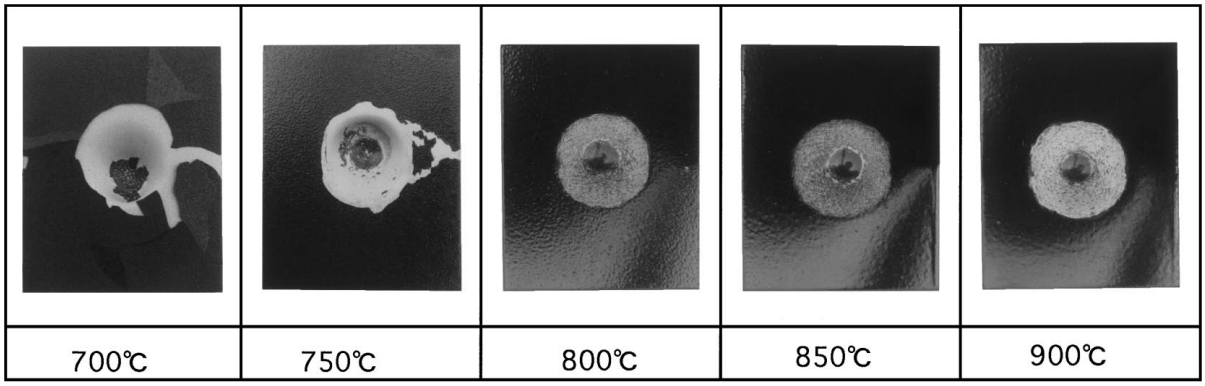

Figure 4 Results of the press test. Figure on the bottom shows the temperature at which the test piece is fierd.

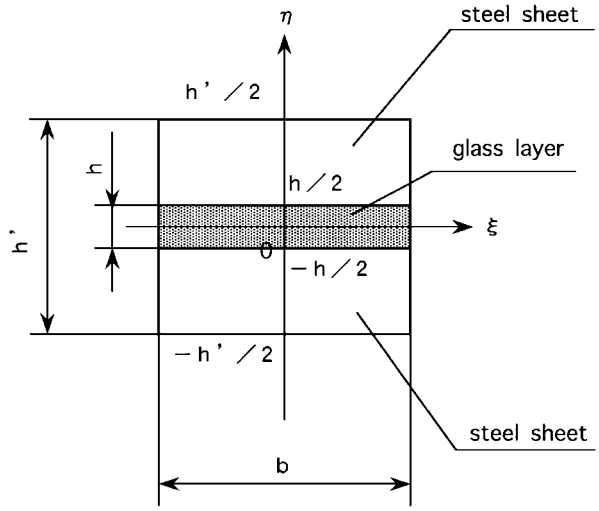

Figure 5 The model of superposition of the test piece. b; width of glass layer. h; thickness of glass layer. h′; thickness of superposition of the test piece.

The moment of inertia of area of the steel sheet, Is, is expressed by:

$$\begin{aligned} \mathrm{Is} &= \int_{\mathrm{h}/2}^{\mathrm{h}'/2} \eta^2 \,\mathrm{dA} + \int_{-\mathrm{h}'/2}^{-\mathrm{h}/2} \eta^2 \,\mathrm{dA} \\ &= \int_{\mathrm{h}/2}^{\mathrm{h}'/2} \eta^2 \,\mathrm{b}\,\mathrm{d}\eta + \int_{-\mathrm{h}'/2}^{-\mathrm{h}/2} \eta^2 \,\mathrm{b}\,\mathrm{d}\eta \\ &= \frac{\mathrm{b}}{12}(\mathrm{h}'^3 - \mathrm{h}^3) \end{aligned} \tag{4}$$

The distance between the neutral surface and the adhered surface on the superposition, ej, is

$$\mathrm{ej} = \frac{\mathrm{h}}{2} \tag{5}$$

Substituting formulas (2), (3), (4), and (5) into formula (1) gives

$$\sigma = \frac{3\mathrm{P}\cdot\mathrm{L}\cdot\mathrm{h}}{2\mathrm{b}} \cdot \frac{\mathrm{Eg}}{\mathrm{Egh}^3 + \mathrm{Es}(\mathrm{h}'^3 - \mathrm{h}^3)} \tag{6}$$

where P = maximum mechanical failing load (N), L = span (m), b = width of test piece (m), h = thickness of glass layer (m), h′ = thickness of superposition area (m), Eg = Young's modulus of glass (Mpa) and Es = Young's modulus of steel sheet (Mpa).

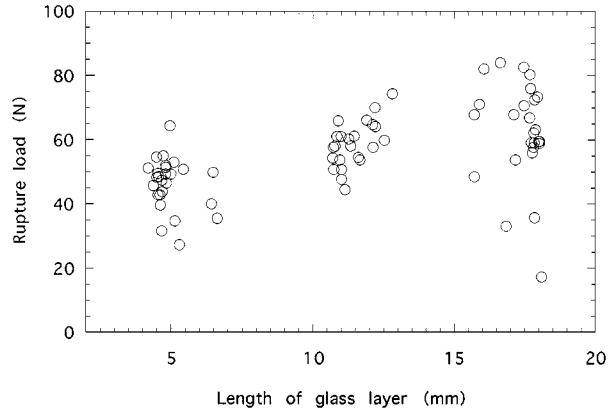

Figure 6 The relation between length of glass layer and rupture load.

The adhesion strength, σ (Mpa), can be determined from formula (6). In the experiment, Young's modulus of glass (frit) was 83300 Mpa on the basis of the measurements made using sound waves and that of the steel sheet at 18 °C was 205800 Mpa.

The test piece must be sized for determining the adhesion strength of vitreous enamel by using the abovementioned formula (6).

The maximum mechanical failing loads of the test pieces were optimized using various lengths of superposition, ℓ. The result is illustrated in Fig. 6. It can be seen that the maximum mechanical failing load fluctuates with the increase in the ℓ value. Although a test piece with extremely short or long superposition is rarely precisely superposed, in a straight line, a test piece with approximately 11 mm of superposition can be stably prepared. The length of superposition, ℓ, was therefore fixed at 11 mm. The glass layer did not fail completely in the test piece with the length of superposition of 20 to 28 mm and the deformation of the steel sheet started from the edge of superposition. Such test pieces were not used in the experiments.

The maximum mechanical failing loads of the test pieces (length of superposition: 11 mm) with glass layers of various thicknesses were measured to determine the optimum thickness of the glass layer, h. The result is illustrated in Fig. 7.

In the test pieces with an extremely thin glass layer, the superposed area was frequently not the same as the adhered area, while in those with an extremely thick glass layer, it was difficult to keep the two steel sheets horizontal and parallel to each other because

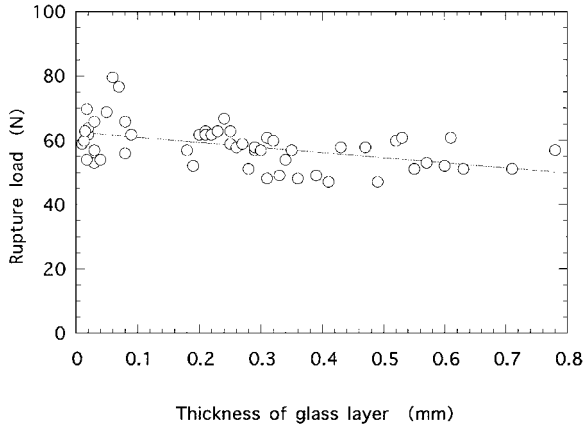

Figure 7 The relation between thickness of glass layer and rupture load.

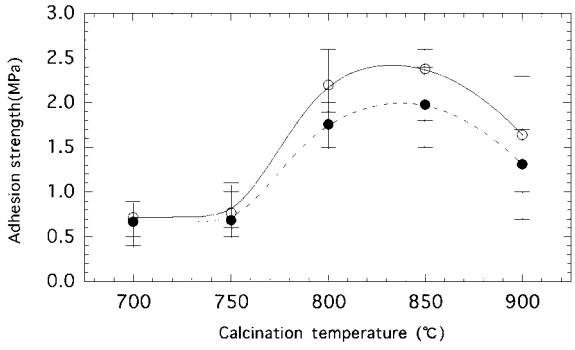

Figure 8 The relation between calcination temperature and adhesion strength. ○ rasped off ● standard.

glass easily flows out from the edge of the superposition area. Thus, stable preparation of the test pieces with a very thin or thick glass layer was difficult. The thickness of glass layer was, therefore, fixed at 0.2 to 0.4 mm. The thickness of the practical ground coat frit for glass-coated steel is 0.2 to 0.4 mm in the same range of the test pieces used for the experiment.

In practice, the surface of the steel sheet is sometimes pretreated by sandblasting to roughen it in the manufacture of vitreous enamel products. The standard test pieces prepared by degreasing only without coating by spraying the ground coat frit were compared with the test pieces prepared by roughening the surface of the steel sheet with #100 sandpaper, degreasing it, coating by spraying the ground coat frit and rasping. The adhesion strength of the standard test pieces, as illustrated in Fig. 4, does not differ from that of the rasped test pieces as checked by the press test.

Then, the quantitative evaluation test was carried out, and the test result is illustrated in Fig. 8. It can be seen that the adhesion strength of the rasped test pieces is generally higher than that of the standard test pieces. This may be because the actual area of adhesion achieved by rasping the surface of the steel sheet is larger than the apparent superposed area. Accordingly, the result can evaluate an adhesion factor which can not be evaluated by the press test.

The adhesion strength increased with an increase in the calcining temperature up to 700 to 800 °C, reached a maximum adhesion strength at 850 °C, and decreased at 900 °C. The result agrees with the trend observed in the press test results.

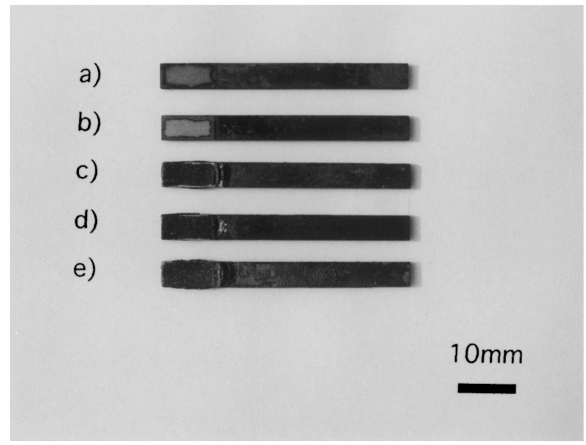

Figure 9 Photograph of destruction surface. The temperatures of calcination were a) 700 °C, b) 750 °C, c) 800 °C, d) 850 °C, e) 900 °C.

Although it is hard to identify the destruction-starting point in the adhered part in the press test because of the permanent deformation caused by this method, the destroyed part can be identified in the present test method. Fig. 9 reveals that the surfaces of the steel sheets are exposed due to the destruction of the interface between the steel sheet and glass in the test pieces calcined at 700 and 750 °C, and that glass from the destroyed glass layer remains on the steel sheet in the test piece calcined at temperatures from 800 to 900 °C, because destruction of the glass layer begins at the weakest part. This is perhaps because the adhesion strength is so much increased by raising the calcining temperature that the adhesion strength of the interface exceeds the strength of glass. This agrees with King's [3] point of view that the adhesion strength between the steel sheet and the ground coat frit is higher than the strength of glass itself.

Our results indicate that vitreous enamel has the adhered layer with a certain thickness.

Our test method is therefore considered to be appropriate for quantitative evaluation of the adhesion strength of vitreous enamel.

Our test method is characterized by the obtaining of objective data without the visual observation necessary in the press test, and employs a simple procedure without using the special tester used for the PEI method. Since the current test methods for evaluating the adhesion strength of vitreous enamel do not have these special features characteristic of this test method, it will be able to be put to practical use for evaluating vitreous enamel.

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