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ON HYDROGEN INDUCED FRACTURE OF PORCELAIN ENAMEL LAYERS

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INTRODUCTION

Hydrogen has been established as a major cause of coating defects when porcelain enamels are applied to a steel base [1]. Fishscales in enamel are small chips or scales which pop loose from the layer after the enamel is cooled [2]. They may appear immediately or they maybe delayed for some time. These particles are half-moon shaped, thin on one edge and thick on the other, resembling the scale on fish. Figure 1 shows a remaining surface of the enamel and its cross sectional view when fishscaled. This defect is only found in enamelled sheet steels and believed to be a localized fracture of the enamel caused by hydrogen gas building up a pressure at the interface between enamel and steel, which is eventually sufficiently high enough to fracture the enamel.

Any hydrogen produced at enameling temperature (usually around 800 - 850°C) can be readily dissolved in the atomic form in steel. When the enamelled steel is cooled to room temperature, however, the steel may have supersaturated and hence rejection of atomic hydrogen into pores, where it recombines to form molecular hydrogen can occur. These pores may be bubbles situated at the enamel-steel interface or may be areas of poor adherence between the enamel and steel. If the volume of hydrogen diffusing out is small, or the pore volume large, then the interface pressure may never reach the critical value required to fracture the enamel.

For many years various investigators have examined the problem of fishscale formation but, as yet, no comprehensive theory has been presented that will explain all the observed features of this serious enameling defect. For a period of years we have been studying the data from many cases of fishscale formation and have attempted to develop a concept of the fishscale fracture process, or perhaps more strictly, to synthesize this concept largely from parts of existing ideas and theories. Although the result of this work may not give complete understanding of this fracture process, it is believed that main outlines of the process can be stated with some confidence.

PROPERTIES OF ENAMEL LAYER [3]

A typical enamel layer with a hot water resistant ground coat applied to an ordinary rolled steel (0.06% C) has been found to possess tensile strength of 77 to 146 MPa and Young's modulus of 34 to 49×10^3 MPa depending on the exact kind of sheet steels and enameling frits used, thickness of enamel and firing conditions. The enameling frits used have tensile strength of 294 to 314 MPa and Young's modulus of 687 MPa when measured in the form of fibre. The difference is mainly caused by the introduction of bubble structure in the enamel layer which decreases the effective enamel volume by 10%. The effect of bubbles on the strength and Young's modulus of enamel

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*Mechanical Engineering Research Laboratory, Hitachi Limited, Japan layer may be discussed by the empirical equation concerning the effect of pore on the strength of ceramics [4] and by the theoretical treatment [5]. Residual stress of the enamel layer was found to be in compressive and ranged from 13 to 23 MPa. When properly fired, the interfacial strength of enamel and steel is considered to be higher than the strength of the enamel itself, because the enamel failed before the interface fails when attempts of interfacial strength measurement were performed. The properly fired enamel shows that iron diffuses from steel into enamel during firing, the distance of diffusion being 100 - 150 μm and that cobalt which is added to promote adhesion between enamel and steel locally precipitates near the interface as shown in Figure 2.

FRACTURE SURFACE OBSERVATIONS

Fishscale chips are usually 1-3 mm long and 70-200 μm thick on thicker edges. A typical fracture surface is shown in Figure 3. Close inspection of many different fishscaled surfaces indicates that there were no definite mirror-mist boundaries observed, instead entire fracture surfaces seemed to be mirror and ripple marks were found on the fracture surfaces. It may suggest that the propagation of a crack proceeded normal to the ripples and the origin of the crack was beneath the observed crack. The presence of ripple marks suggests that fracture occurs catastrophically and ripples are usually observed on impact fracture surface of glass. According to the mirror radius-stress data on annealed plate glass [6], mirror areas of fracture with radius ranged from 0.5 to 1.5 mm correspond to the tensile stress of 55 to 100 MPa, which is in the range of the strength of the enamels.

MECHANISM OF ENAMEL FRACTURE BY HYDROGEN

Hydrogen generated during enamel firing dissolves into steel in the atomic form and the amount of hydrogen generated and dissolved may depend on kinds of steels, enameling frits and ingredients used, firing conditions and other factors [7]. Our measurement showed that 7.41 x 10^{-3} mol/m² of hydrogen dissolved into a hot rolled 0.06% C steel fired at 850° C for 5 minutes in Ar atmosphere with a hot water resistant ground coat two side enameled (300 μm thick). This corresponds to 0.95 ppm hydrogen accomodated into the steel of 2 mm thickness.

When this enamelled steel is quenched from 850° C to room temperature without allowing hydrogen to diffuse out of the steel, at room temperature excess hydrogen (H concentration at 850° C, C_H - equilibrium H concentration at room temperature, C_{eq}) has to diffuse through iron lattice and reach the steel-enamel interfaces, where hydrogen precipitates into a void, resulting in H_2 molecules. The diffusion of hydrogen toward the void and precipitation at the void surface may be described as follows [8]. The number of hydrogen molecules, n, precipitated into the spherical void with a radius, r_o, in a unit time is

$$dn/dt = 4\pi r_o^2 J \qquad (1)$$

$$J = D_H[C_H - C_{eq}][1/r_o + 1/\sqrt{\pi D_H t}] \qquad (2)$$

where D_H is diffusion coefficient of hydrogen in the steel. Provided that $r_o \simeq 1\mu m$, $D_H = 8 \times 10^{-9} m^2/s$, $t = 1$ sec, $1/r_o \gg 1/\sqrt{\pi D_H t}$ gives

$$dn/dt \simeq D_H [C_H - C_{eq}] 4\pi r_o \qquad (3)$$

Assuming that hydrogen in the void behaves as an ideal gas, the pressure in the void is given by $P_H V = nRT$. Since the volume of spherical void can be regarded as pressure independent, the rate of pressure build up is

$$dP_H/dt = (RT/V)dn/dt = (3D_H RT/r_o^2)[C_H - C_{eq}] \qquad (4)$$

C_{eq} is given by the sum of H trapped in the steel (0.02 ppm) [9] and equilibrium solubility at an equilibrium H pressure corresponding to a fracture stress of the enamel (0.02 ppm) calculated from Phragmen's equation [10], and then we obtain

$$dP_H/dt \simeq 210 \text{ MPa/sec} \qquad (5)$$

This value exceeds the strength of the enamel layer and this loading rate is very large even compared with ordinary tensile test of steel materials and it is believed that it corresponds to an impact loading for brittle materials such as enamels. This and fracture surface observations led us to suggest fishscales as a result of impact fracture due to hydrogen pressure build up at the steel-enamel interface.

The fishscale fracture due to impact loading may be treated similar to spalling or scabbing of flat plates by detonation [11]. The hydrogen pressure build up at the interface may be assumed to be a saw toothed compressive pulse and to pass through the enamel without change in shape or intensity. If its maximum intensity is σ_m, then as it is reflected at the surface of the enamel, its sign is changed to become tensile. Figure 4 shows the individual incident compressive and reflected tensile waves and their net effect at time t = 0, $(1/4)\ell/c$ $(1/2)\ell/c$ and ℓ/c, where ℓ is the thickness of the enamel and c is the velocity of the pulse, as they approach the surface. The figure shows that the greatest tensile stress (σ_m) first arises at one half the thickness from the enamel surface. Tensile stress σ' in a typical plane is given by

$$\sigma' = \sigma_m[1-(\ell-2x)/\ell] = (2x/\ell)\sigma_m, \qquad x \leq \ell/2 \qquad (6)$$

When the tensile stress reaches fracture stress of the enamel, σ_f, then fracture will occur in the enamel in a layer where σ_f is first reached. According to the pressure build up, fracture will occur at a distance $\ell/2$ from the surface or less, or not at all. If fracture occurs, then the enamel above the fracture surface will have trapped in it an amount of upward momentum, which causes the enamel chip to fly off. This agrees with the observation in which fishsclaes always occur at a distance less than a half of the enamel thickness from the surface. The size of fishscale is considered to vary roughly in proportional to the amount of energy available for fracture which is confirmed by AE monitoring discussed below.

In order to see if the catastrophic failure of a completely brittle material such as enamel produces acoustic emission signals just prior to fracture, enamelled steels were cathodically charged with hydrogen while any acoustic signals generated were recorded. The recording traces of the transducer outputs showed only electronic noise preceeding the very large signals generated by the onset of catastrophic crack growth (fishscale). This agrees with the result of AE monitoring of glass fracture which shows AE only from the rapid propagation of macrocracks [12]. Typical data obtained during hydrogen charging are shown in Figure 5. Close inspection reveals a direct correlation between the number of AE bursts and the number of fishscales formed and also that the larger chip emits more acoustic event than a smaller one.

CONCLUSION

A rate of hydrogen pressure build up at the steel-enamel interface is very important for delayed fracture of enamels. When the rate is very high, the loading by the pressure build up against the enamel becomes close to that of an impact type and the reflected tensile wave will cause fracture at a distance less than half of the enamel thickness from the surface. The fractographic observation, AE monitoring and many fishscale formation data support the above hydrogen induced impact fracture mechanism.

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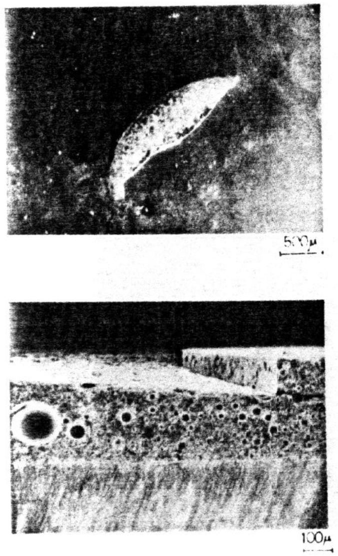

Figure 1 An Example of Fishscale

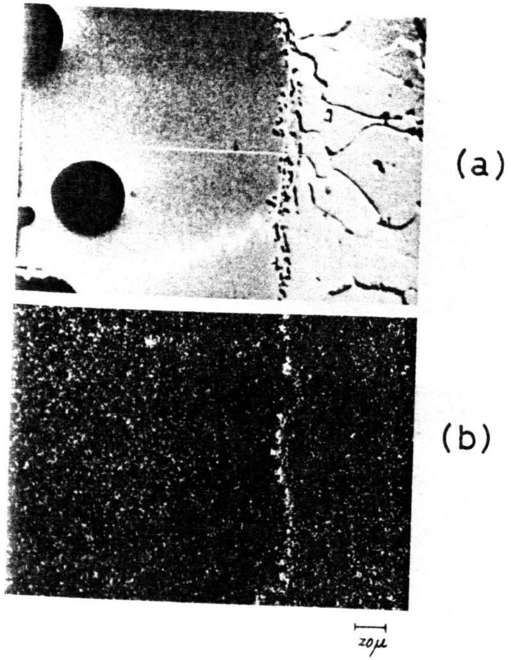

Figure 2 XMA Result of Steel-Enamel Interface
(a) Fe Line Profile
(b) Co X-Ray Image

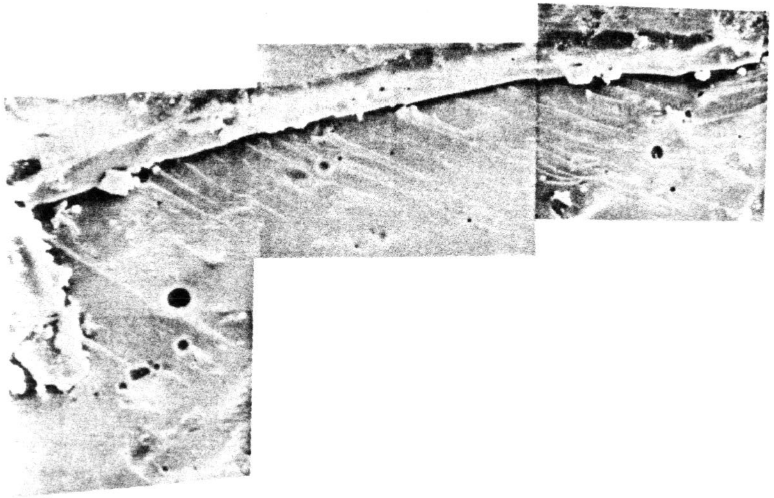

Figure 3 Fishscale Fracture Surface

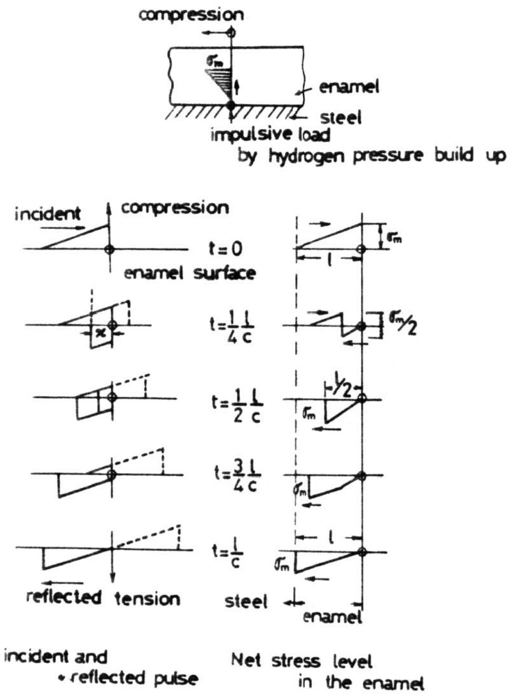

Figure 4 Impact Loading of Enamel Layer at the Steel-Enamel Interface

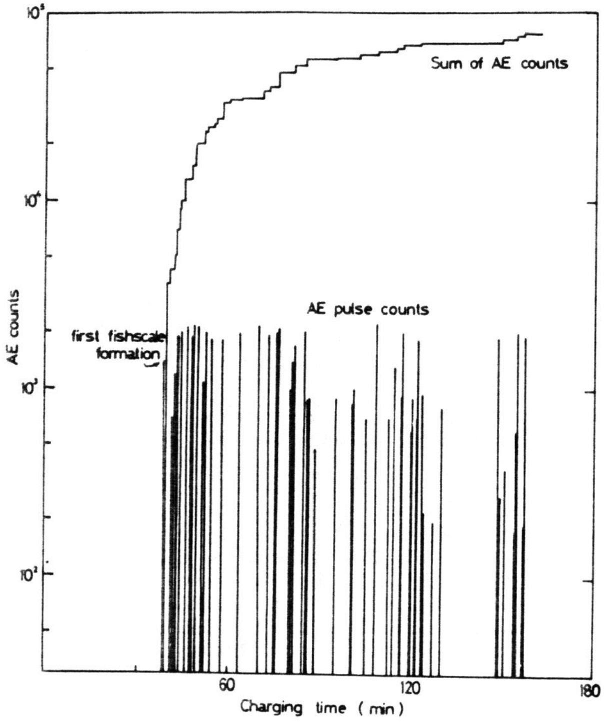

Figure 5 An Example of AE Monitoring During Hydrogen Charging