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The presence of an iron oxide layer at the enamel/steel interface in one-coat porcelain enamelling

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The chemical measurement of the iron oxide present in the enamel was not in agreement with the iron oxide content calculated from diffusion profiles. This discrepancy could only be explained by assuming that a layer of iron oxide about 1 μm thick was present at the interface. An examination of the phenomena associated with this type of enamelling, the constant rate of oxidation and the saturation of the enamel at the glass/steel interface, has led to the conclusion that such an oxide layer must be present.

1. Introduction

Although the overall mechanism involved in the vitreous enamelling of ferrous metals is understood, there is still considerable doubt over many of the details. The role of the adhesion oxides, CoO and NiO, in the ground coat enamels is difficult to explain, particularly when consideration is also given to the nickel flash required in the direct-on system [1]. Similarly, although the basic cause of the defect known as "fish-scaling" was identified some time ago, its occurrence is both sporadic and unexplained.

The existence of an oxide layer at the enamel/steel interface has also been debated for a long time. The evidence was reviewed by King *et al.* [2], who were against the concept, and more recently by Dietzel [3] who is in favour of such an oxide layer. The requirement of an oxide layer in the initial stages of firing to promote wetting appears to be accepted by most authors; the problem concerns the subsequent survival of this layer when the enamelling reactions are completed. Most of the previous evidence is indirect such as contact angles, and this work is the first quantitative demonstration of the oxide layer and its extent.

Some time ago an investigation was made into the reactions which occur in the one-coat enamelling system [4]. Although there were many practical difficulties to be overcome in making the necessary measurements in this very complex system, two stages of oxidation were identified and diffusion profiles measured for the movement of the iron oxide into the enamel layer. From this data a diffusion constant for the iron oxide was calculated and the amount of iron present in the enamel determined chemically. There were discrepancies between the amount of iron oxide in the enamel as determined chemically and calculated from the diffusion data. Both methods were checked in great detail but the only satisfactory interpretation of the results was that a layer of iron oxide was present at the enamel/steel interface.

A reconsideration of this problem has indicated that this oxide layer must be present to account for other features which occur in this system. The methods used for the measurement of the

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iron oxide content of the system are central to the main thesis of this paper and have been given in considerable detail, including the many checks which were made of their validity.

2. Experimental procedure

2.1. Materials

The enamel frit, the steel and the pretreatment of the steel have been described previously [5]; in this series of experiments the samples were 1.7 cm by 2.5 cm in size.

2.2. Application and firing of the enamel

Six specimens were fired simultaneously on a jig which was drawn into the furnace at 0.33 cm $\sec^{-1}$. After being held in the hot zone for a predetermined number of seconds the jig was automatically drawn out of the furnace at the same speed. If the jig was not halted in the hot zone a firing time of 36 sec was recorded. With the furnace wall temperature controlled at 850° C the specimens attained a firing temperature of 805° C. The latter was recorded for each firing by a travelling thermocouple.

2.3. Determination of iron

The fired enamel was removed from the steel using a percussion mortar; the average loss of enamel in this procedure was shown from eight experiments to be 0.53 % by weight. The recovered enamel was then dissolved in a mixture of sulphuric and hydrofluoric acids and the iron content determined colorimetrically using the o-phenanthroline method [6]. The iron content of the enamel slip and the contamination which occurred during the stripping procedure were measured in the following manner. A quantity of slip was fired for 300 sec in a platinum crucible at 805° C and then divided into two parts. One was crushed in the percussion mortar, which also contained a pretreated steel blank; the other was crushed in an agate mortar. The average FeO content values from four determinations by each method were 0.123% and 0.118%, respectively, indicating that FeO pick up from the steel and mortar was 0.005%. All the results given are the mean of four specimens which were fired at the same time. As the spread of results for each point (expressed as a percentage) was similar, the standard deviation was calculated normalizing the results from four firings and therefore, is based on sixteen specimens. The results have been expressed as FeO per unit area, and corrections applied for the iron content of the enamel, the contamination from the mortar, and the edges and hole of the specimen.

2.4. Determination of diffusion profiles

Four different polishing methods were tried for the preparation of suitable specimens for electron probe examination. In every case oblique illumination under the optical mircoscope revealed relief polishing, making the specimens unsuitable for probe analysis. This problem was overcome by removing the steel from the enamel by grinding, followed by treatment with hot 2 N sulphuric acid It was shown experimentally that the loss of iron oxide arising from this acid treatment was less than 2% of the iron oxide concentration at the interface. Twelve pieces of the enamel were then bonded together and mounted and polished in the usual manner. "Standards" were prepared by smelting ferrous oxalate into the enamel at 1200° C and the melt was poured into a metal 1 cm diameter by 4 cm long. The central slice, 5 mm thick, was used for the electron probe study and two adjacent thinner slices taken for chemical analysis.

Obtaining diffusion profiles was difficult because of the bubbles and ilmenite crystals which are always present in the enamel samples. To overcome these difficulties the areas were carefully selected and an integrated count taken over an area 6 μm^2. Iron diffusion profiles were taken for two samples from each firing as shown in Fig. 1.

The distribution of some other elements, sodium, potassium and titanium, across the specimens was investigated but as no differences in the concentration were found the data will not be reported. Attempts to demonstrate nickel in the enamel were unsuccessful.

2.5. Interface examination

Attempts to expose the interface using organic solutions of iodine were unsuccessful [7]. The method was satisfactory for other types of steel but could not be made to work on the low carbon steel used here. Some success was achieved by sticking the sample to a metal block with an epoxy resin and then deforming the low carbon steel by repeated impact. After a time it was possible to strip the steel leaving the enamel adhering to the metal block. Some chipping of the exposed enamel/steel interface always

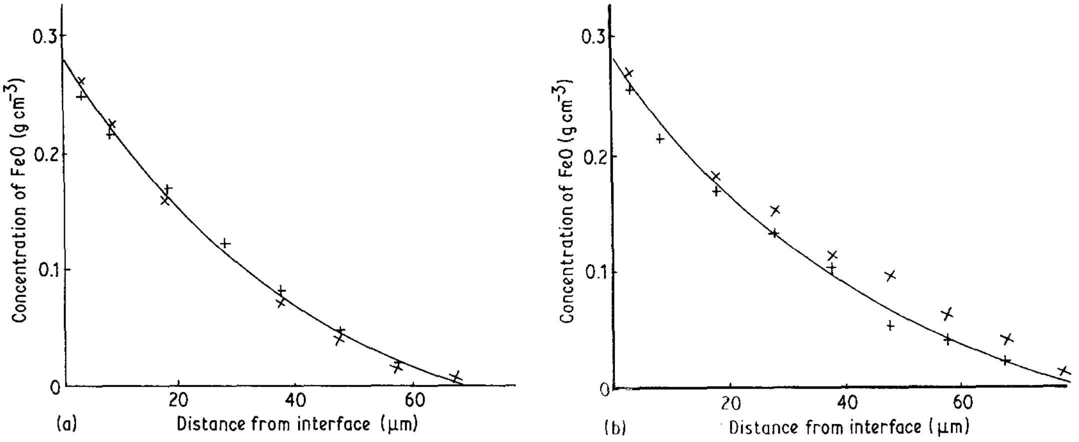

Figure 1 Diffusion profiles of FeO in enamel at 805° C: (a) at a firing time of 540 sec, (b) at 770 sec. Points from two specimens on each profile.

occurred. This was indicated by the exposure of the white enamel below the dark interfacial zone. Specimens with less than 20% of the interfacial area damaged were used for X-ray examination. The metal block was designed to fit the specimen holder of the X-ray goniometer and the routine work was done using Cu$K\alpha$ radiation. The more important findings were checked using molybdenum radiation because of the possibility of interference from fluorescence.

3. Results

Specimens were fired for various times ranging from 36 to 1200 sec and the iron content of the enamels determined as described. Even with the shortest firing time, 36 sec, the enamel had fired down to a smooth finish but the most satisfactory appearance was obtained with firing times of 180 to 300 sec. The curve of iron content against time appears linear up to 1200 sec, curve A in Fig. 2, indicating a continued oxidation after fusion of the enamel frit.

The diffusion profiles for twelve firing times up to 1800 sec were measured and two examples are shown in Fig. 1. Values for the concentration of the FeO at the interface were taken from the diffusion profiles and since there was no trend with time, as shown in Fig. 3, the average value 0.283 g cm^{-3} was used for calculating the diffusion coefficient. This constant surface concentration C_0 indicates that the diffusion of FeO into the enamel can be treated as a simple case

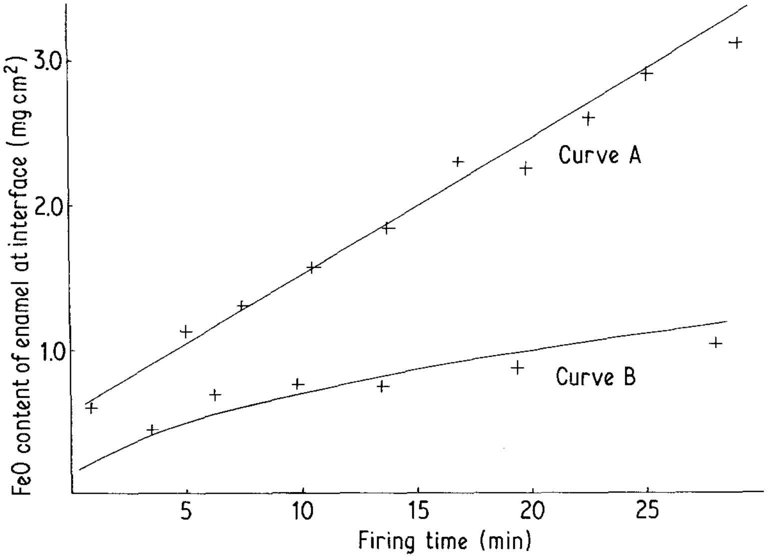

Figure 2 Measurement of FeO in enamel layer. Curve A best fit straight line to experimental points from chemical determination. Curve B continuous curve calcualted from diffusion coefficient with experimental points from diffusion profiles.

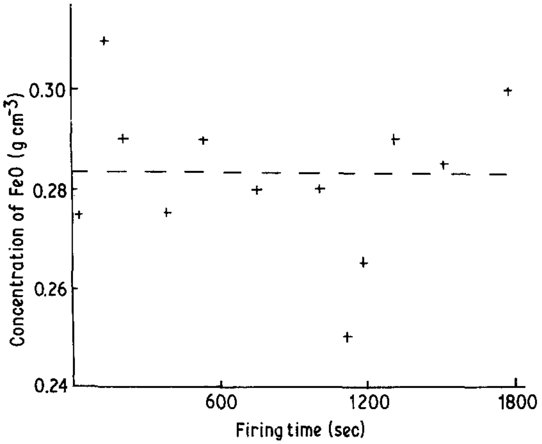

Figure 3 Variation in estimated values from diffusion curves for FeO concentration at the enamel/steel interface at 805° C.

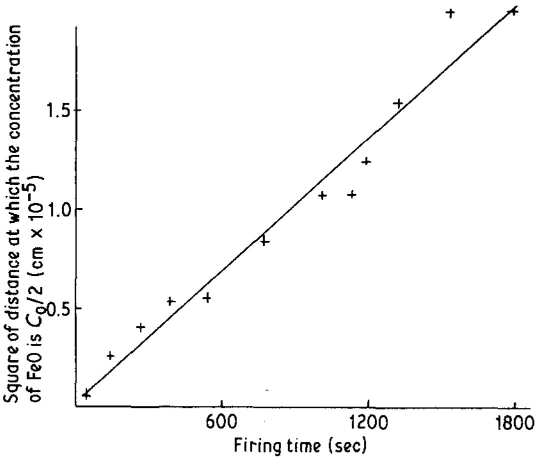

Figure 4 The plot of (x'^2) against time, see Equation 2, at 805° C.

of diffusion into a semi-infinite medium:

$$C(x, t) = C_0\{1 - \mathrm{erf}\,[x/2\,(Dt)^{1/2}]\} \qquad (1)$$

where x is the distance of penetration and t is time. This permits the estimation of the diffusion constant D which in turn enables the amount of FeO taken up by the enamel to be calculated.

From the diffusion profiles (see Fig. 1) the distances of penetration x' were measured where the FeO concentration is $C_0/2$. The diffusion coefficient can then be calculated from Equation 1:

$$\mathrm{erf}\,[x'/2\,(Dt)^{1/2}] = 1/2, \quad \text{or}\; x'/2\,(Dt)^{1/2} = 0.48,$$

$$\text{or}\; (x'^2) = 0.92\,Dt. \qquad (2)$$

Therefore the plot of (x'^2) against time should lead to a straight line from which D can be calculated. From Fig. 4 a diffusion coefficient of 1.3×10^{-8} cm^2 sec^{-1} can be estimated for 800° C.

The amount of FeO (M_{FeO}) that diffuses into the enamel is given by: $M_{\mathrm{FeO}} = 2C_0(Dt/\pi)^{1/2} = 3.6 \times 10^{-5}\,t^{1/2}(\mathrm{sec})\,\mathrm{g\,cm^{-2}}$. This curve is shown in Fig. 2 and is labelled B. The individual points, plotted adjacent to this curve, are estimates of the iron content of the enamel obtained from the areas under the individual diffusion profiles.

The difference between curves A and B in Fig. 2 is obviously much greater than the experimental error and it appeared probable that the explanation is associated with the two methods of specimen treatment. For curve A the enamel on the specimens was removed mechanically down to the surface of the metal, and all the removed analysed for iron. The specimens for curve B were treated in the reverse manner; the metal was removed down to the surface of the enamel. Therefore, if any iron oxide was present between the steel and the enamel, it would be found by the first method of analysis but not the second.

Then the amount of iron present at the interface was calculated from the difference between curves A and B, i.e. this amount corresponds to the net increase of FeO at the enamel steel interface. Taking the density of the FeO as 5.75 cm^{-3} and assuming an even distribution over the apparent surface area, the thickness of the oxide layer can be calculated as a function of the firing time, see Fig. 5.

Attempts to demonstrate this layer by X-ray diffraction were unsuccessful; only in the case of the specimen fired for 430 sec was the main wustite peak found. There could be many reasons

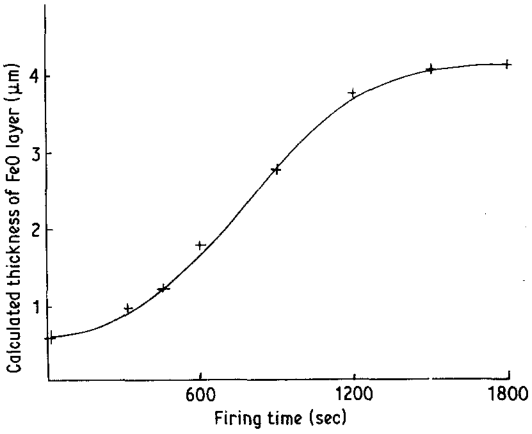

Figure 5 Calculated thickness of oxide layer at interface.

for this; the amount is at the limit for X-ray detection, the iron oxide may not be fully crystalline and in the separation of the two surfaces the oxide may become divided between the two surfaces.

Three other crystalline phases were found at the interface, anatase, rutile and ilmenite; all appeared randomly oriented.

4. Discussion

Lefort and Friedberg [8] have studied the high temperature oxidation of enamelled steel after the initial firing. They found a linear oxidation rate, that the mechanism was atmospheric oxidation and that the limiting factor was oxygen diffusion through the enamel. The relevant oxidation rates they found are considerably lower than those reported here but this is probably due to the different conditions and enamel composition.

Extrapolation of the curve indicates that approximately 5.6 $\mathrm{g\,m^{-2}}$ of iron oxide is formed before the enamel fuses and that with a normal industrial firing time of 5 min in the hot zone a further 7.0 $\mathrm{g\,m^{-2}}$ after the enamel has fused.

The errors associated with the calculation of the diffusion coefficient have already been mentioned but despite this the value is in reasonable agreement with the work of Borom and Pask [9]. Extrapolation of their data on the diffusion of $\mathrm{Fe^{2+}}$ in sodium disilicate glass to the present firing temperature (800° C) gives a value of $1 \times 10^{-8}\ \mathrm{cm^2\,sec^{-1}}$.

The shape of the diffusion curves, the constant concentration of FeO at the interface, together with the successful application of the diffusion constant used to calculate the mass flow indicate that the correct solution of Fick's Law has been used. Other workers using more conventional techniques have reported curves appropriate to the "thin film" solution rather than the "constant source" [10].

The difference between the two curves in Fig. 2 indicates that iron oxide is present at all firing times and the amount increases with time. The most important region is that between 200 and 300 sec which is the normal firing time. From a statistical point of view the point at 250 sec on the lower curve is separated from the upper curve be eight standard deviations, four from each source. Therefore, it follows that there is a real difference between these two curves over this important region.

If this interpretation of the experimental data is correct, then there are three phenomena which require explanation: the saturation of the enamel with iron oxide at the interface, the presence of a layer of iron oxide between the enamel and the steel, and the linear rate of oxidation shown by curve A in Fig. 2. The thermodynamic requirement for the saturation of the enamel with iron oxide is the presence of excess iron oxide at all times and the experimental data given here support this concept. It is suggested that, when the enamel fuses, there is already a layer of iron oxide, approximately 1 μm thick, present on the steel surface and the oxidation continues with iron diffusing through the iron oxide layer. Thus although it is convenient to divide the oxidation of the steel into two stages, before and after the enamel fuses, the overall process is probably similar and the oxide formed in the first stage is not dissolved in the enamel before the second stage begins.

Before discussing the linear oxidation rate which was found, it is necessary to emphasize the assumptions involved in the calculation of the curves shown in Figs. 2 and 5. Although the scatter of the points about the curves is a reasonable indication of the experimental errors involved, there is more uncertainty over the reacting surface area which is being measured. The various factors involved are shown in Table I.

In view of the uncertainty of the actual area

TABLE I Factors affecting the effective surface area available for reaction

Factor	Description	Effect
Acid etch	Metal pretreatment	Increase
Nickel flash	Metal pretreatment	Decrease
Corrosion of metal by enamel	Second stage oxidation	Increase
Diffusion of nickel	Diffusion of nickel into steel at 800° C	Increase
Heterogeneity of steel	Rate of corrosion differs from area to area	Doubtful
Scaling	Discontinuous nature of corrosion reaction	Doubtful

involved at the various times of oxidation, the most reasonable assumption is that the linear rate over the 20 min period resulted from a combination of various mechanisms such as diffusion and the changing area available for reaction. This latter factor would be important if the controlling mechanism were a surface reaction.

The interpretation given above appears to account for the three factors mentioned but in addition appears to account for another phenomenon which is always found in one-coat enamelling. This is the presence of what appears to be small particles of detached metal adjacent to the enamel/steel interface. These are invariably present in such numbers that a mechanism for their production is required which is more probable than the accidental undercutting of the metal by the enamel.

Such a mechanism could arise from the presence of a layer of iron oxide at the enamel/steel interface; the diffusion of the iron atoms through the subsequent condensation of the vacancies remaining behind to form cavities. The molten enamel then breaks through into the cavities and portions of the oxide become isolated in the enamel layer. Most stages of this sequence can be observed in micrographs of enamelled specimens indicating that on average just one layer of oxide has been destroyed in this manner in a normally fired enamel.

Two major reasons have been advanced by workers in this field against the presence of an oxide layer at the enamel/steel interface; the first is that such a layer is difficult to demonstrate using either microscopy or X-ray diffraction and the second, that such a layer would be very weak and result in a poor bond between the metal and ceramic layers. The first objection may be overcome by pointing out that some workers have reported oxide layers [11] and that a layer of oxide in the region of 1 μm thick would be difficult to demonstrate, especially when the material is not in one plane but convoluted and following the line of the interface. Additionally the oxide layer may not be crystalline and may become rapidly impure as the enamel component begins diffusing into it.

The other reason advanced against the presence of an oxide layer, the poor mechanical strength of such oxide films, appears a rather less serious objection. Work by Peters and Engell [12] showed that the adherence of a wustite film formed at 800° C increased as the thickness of the film decreased. They found values in excess of 10 MNm^{-2} with films 100 μm thick.

Acknowledgements

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