Effect of industrial process parameters on fishscale: Electrolux Italia experience

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Abstact

The work is aimed at studing the influence of manufacturing parameters on enamelling quality in order to prevent fishscale occurrence. The research is a collaboration between Letomec srl and Electrolux Italia spA and it was conducted on steel samples representative of the materials employed in Electrolux products. The work involved experimental activities (electrochemical permeation, hydrogen content measurement and metallographic examinations) to evaluate the properties of the steel significant for the fishscale resistance. Fishscale susceptibility was investigated considering enamelling baking temperature, dew point of furnace, steel quality and the type of enamel.

Introduction

The steels used for enameling need to have specific properties, in particular, the following conditions must be satisfied:

- to guarantee the efficacy of the adhesion between enamel and steel;
- to provide a good deep drawing capability;
- to show a significant hydrogen trapping activity.

Typically, low carbon steels are used for vitreous enameling. The low carbon content is reached either by decarburising the steel at the solid state (open coil steels) or by removing carbon when the steel is in the liquid state (Interstitial Free). The porcelain (vitreous) coating is applied to the steel by a high productivity industrial enamelling process that can be affected by several defects among them the fishscaling. that is considered the most dangerous damage in the production of enamelled steel products [1]. Fishscaling is caused by an excess of hydrogen content in the steel that is produced during enamel firing at a temperature of 800-850°C when hydrogen dissolves into the steel. The solubility of the hydrogen in steel strongly decreases during subsequent cooling but the hydrogen present tends to slowly migrate towards the enamel-steel interface. In the interface region hydrogen concentrates as the ceramic layer prevents the diffusion, thus producing high pressure. As a consequence small chips of enamel pop loose from the layer even after a long time after the end of the product manufacturing [2]. Steel susceptibility to fishscale depends on its microstructure in particular on the content, distribution and nature of site traps that are available for trapping the hydrogen thus peventing its diffusion toward the surface. Although fishscale is a subject of many researches since '40s [3], and a wide amount of works is available [4, 5], first contributions to a better scientific interpretation of the phenomenon date back to '90s [6,7]. More recently [8, 9], it was demonstrated that steel resistance to fishscale strongly depends on specific parameters both of manufacturing process and chemical composition of the steel. Taking into account the influence of trapping on the diffusion process, fishscale resistance is evaluated by measuring the tendency of the steel to retain hydrogen under controlled electrochemical permeation. In the present state-of-the-art, the most common technique for fishscaling assessment is that defined by the standard EN10209 [10]. The standard uses the “TH” parameter (a function of the breakthrough time, t0) to determine the fishscale susceptibility of steels. If TH is higher than 100 (UNI EN 10209) the steel is suitable for enamelling. However, the discussion about the best method of evaluating enamellability is still open. On the one hand, the breakthrough time is the simplest method to get an indication of steel susceptibility to fishscaling on the other hand, the method is not valid for some steels (for instance for Titanium and Boron steels). Moreover the method is based on a partial measurement of the permeation curve, so it does not provide specific indications on steel trapping ability. In the present work a new device is used with the aim at overcoming these limits. The new technology is the results of a collaboration between Electrolux Italia SpA Forlì and Letomec Srl (a recently founded spi- off of the University of Pisa) and is based on a solid-state sensor for hydrogen measurements. A series of experiments were conducted to study the influence of variables, sheets, type of enamel in industrial enameling conditions (dew point, furnace's temperature), on fishscale susceptibility.

Methods/Discussion

Materials

An Al-killed low Carbon EK steel (UNI EN 10209), and an ED steel (decarburized open coil) were tested. These steels were placed in an enameling furnace of Electrolux appliance plants in Forlì, and submitted to an enamelling process, in accordance with the common industrial procedures used in the process. Two parameters of enamel process were measured: dew point and cooking temperatures. DRAGER® vials were used for measuring dew point temperature, which resulted about 8°C-10°C while cooking temperature resulted in the range 830°C-840°C. Some samples were submitted to an enamelling process on both sides, to fix the hydrogen content by the process itself. Others samples were submitted to an enamelling process only on one side in order to perform forced fishscale by electrochemical hydrogen charging.
Three types of enamels were considered:

- industrial enamel, denominated as "B",
- test enamel, denominated as "D",
- high viscosity enamel, denominated as "F".

Permeation tests on not emmelled specimens were performed to evaluate the hydrogen diffusion coefficient through the as-received steel. Permeation tests, on samples enamel on a side, were performed to evaluate the breakthrough time. Diffusible hydrogen content was measured in specimens, with enamel on both side of the steel, to assess the hydrogen content that dissolves into the metal during enamel firing; these tests were performed using HELIOS III (Patent Pending N. PI2012A000109 by Letomec srl) at 400°C, enamel was removed mechanically before starting the measurement. The samples for permeation tests were prepared with scotch brite grit, under the lubrication of ethyl alcohol, degreased with acetone and dried in air. Specimens for permeation experiments were 50x100mm plates, with a thickness ranging between 0.50 mm to 0.65 mm.

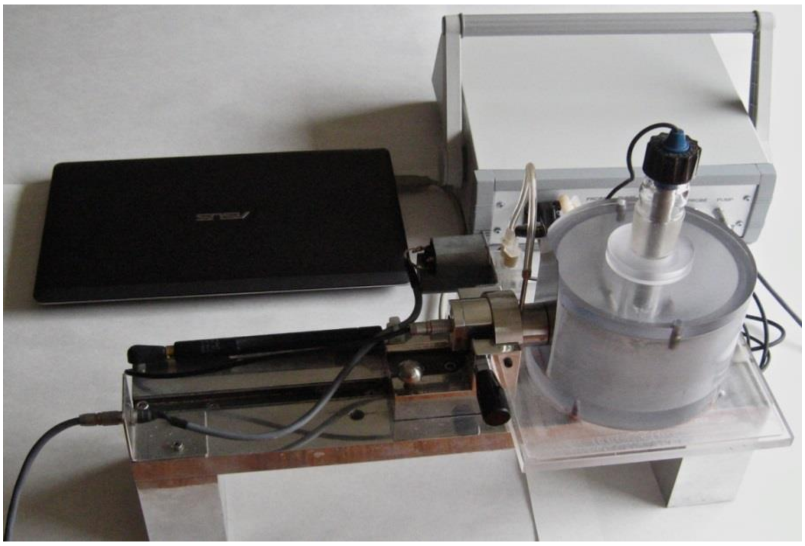


Figure 1: HELIOS apparatus for permeation test.

The test solution was a mixture of 1N H_2SO_4 and tracks of Sodium thiosulfate pentahydrate dissolved in distilled water. Sodium thiosulfate pentahydrate was chosen as hydrogen recombination poison, because it promotes the adsorption of hydrogen through steel. It is worth noting that Sodium thiosulfate pentahydrate is a substance not restricted by the current REACH

norm (as arsenic, or mercuric chloride). The charging current density was kept at 10mA/cm^2, a level that is lower than the value recommended by EN10209 thus avoiding the onset of damage in the metallic membrane [11]. All the reagents were of analytical grade. As shown in Figure 1, the hydrogen permeation tests were conducted using HELIOS II (Letomec's pending patent N. PI2012A000109 by Letomec srl) thanks to its immediate and simple use.
The main components of HELIOS II can be seen in Figure 1: the electrochemical cell contains the test solution, the steel sample, as an active electrode, is located between the probe and the cell, an area of 3.14cm^2 is exposed to the solution inside the container. As observed, test solution doesn't contain Arsenic or Mercury compounds which are indicated by EN10209 but restricted by the current REACH norm. The anode is a platinum coated titanium electrode. During the electrochemical permeation, hydrogen atoms are produced inside the cell, on the steel surface, adsorbed and diffused through the membrane and eventually desorbed from the other surface. A probe, containing a solid state hydrogen sensor, is located on the external steel surface in order to measure the flux of permeating hydrogen by a proper conditioning and recording device controlled by a dedicated Personal Computer. All the experiments were performed at room temperature. Diffusible hydrogen content in specimens with enamel on both side of the steel, was measured using HELIOS III. HELIOS III is a device derived from HELIOS II, and it measures the hydrogen content in metallic samples by hot extraction. In this case, the sample is heated 400°C in order to produce the required desorption. Similarly as HELIOS II, HELIOS III is equipped with a solid state sensor but it is connected to a ceramic chamber where the sample is located to be desorbed.

Calculation

HELIOS II is connected to an electronic control and a dedicated PC for data elaboration and acquisition. Once acquired, the signal, that depends on the hydrogen flux in the examined component, is processed by proper mathematical codes to assess the parameters related to hydrogen diffusion and the corresponding material permeation properties.

Results

Permeation test on not ammelled samples. Figure 2 shows HELIOS permeation curves, obtained for ED and EK samples.

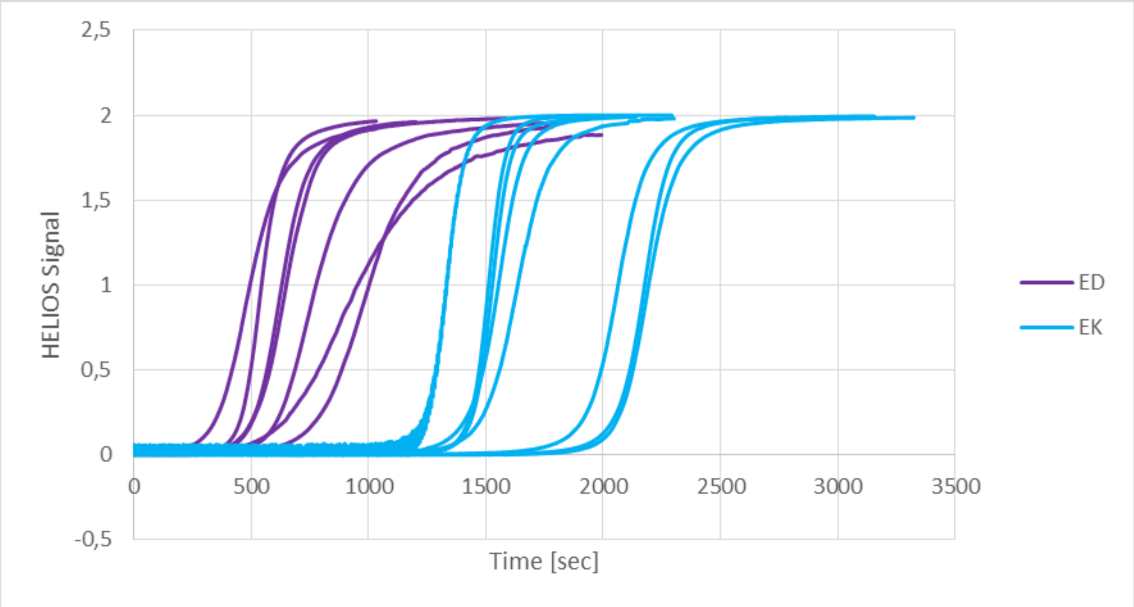


Figure 2: Permeation test performed by HELIOS II of naked steels.

Hydrogen diffusion coefficient was measured by means of several permeation tests, the average value in the ED steel resulted 5.6 10^{-7} cm^2/sec with a standard deviation of 1.3 10^{-7}cm^2/sec. The average hydrogen diffusivity for the EK steel measures 4.2 10^{-7} cm^2/sec with a standard deviation of 1.6 10^{-7} cm^2/sec.

These results, compared with others in the literature [11], indicate that the risk of fishscaling is negligible. From the industrial side, in fact, these materials did not show any fishscale defect. The critical value of hydrogen diffusivity for producing a significant risk of fishscaling in steel is the order of $2*10^{-6}$ cm^2 / sec.

Permeation test on enamelled steels

The comparison of tests on different enamels is reported in Figures 3 and 4. Table 2 reports the values of breakthrough time. The effect of different layers is clearly visible in terms of the hydrogen peak measurement, t_0.

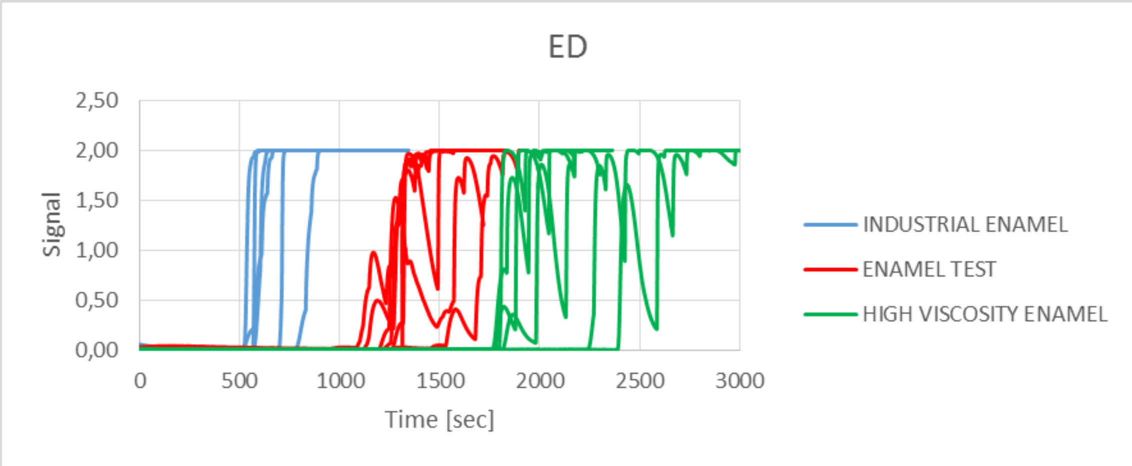


Figure 3: Permeation test performed by HELIOS II of ED enameled steel.

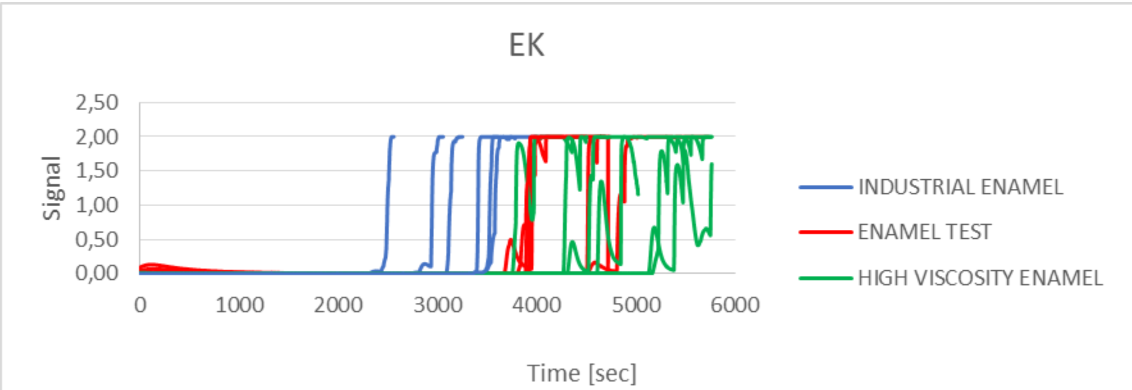


Figure 4: Permeation test performed by HELIOS II of EK enameled steel.

In accordance with the Figures, the breakthrough time can considerably differ with the same steels; this phenomenon can be explained by considering different vitrification and adhesion of the enamel.

Figure 5 shows a section of a sample, exposed to a forced fishscale during electrochemical charging. The fishscale defects visible in Figure 5 have the same orphological characteristics of the fishscale defects produced in industrial enamelling process [12]. As an illustrative example, a sample after the hydrogen permeation test is shown in Fig. 6.

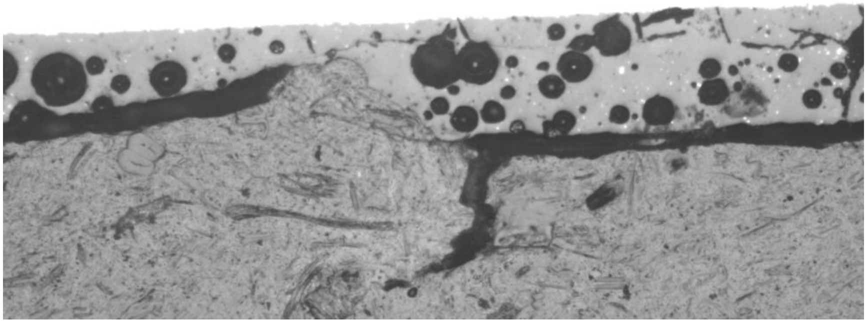
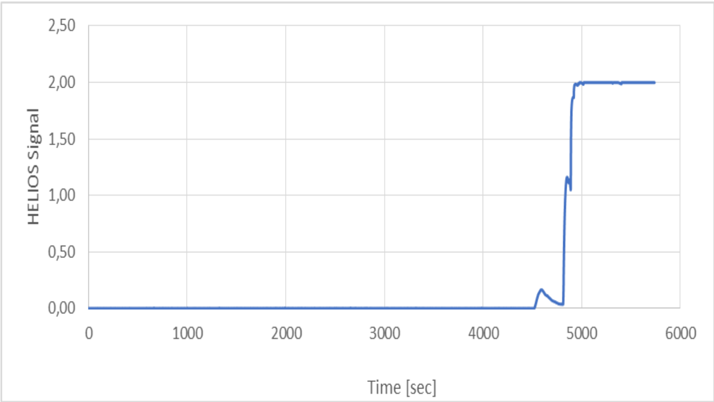


Figure 5: Optical metallography, after hydrogen permeation test, of a Fishscale defect on enamelled surface on ED sample (10x).

Table 1: ***Breakthrough time for each enamelled steel.***

	Industrial Enamel		Enamel Test		High Viscosity Enamel	
	t_0 [sec]	Standard Deviation	t_0 [sec]	Standard Deviation	t_0 [sec]	Standard Deviation
ED	601.5	112	1233.5	118	1931	279
EK	3037	440	4031	383	4548	543



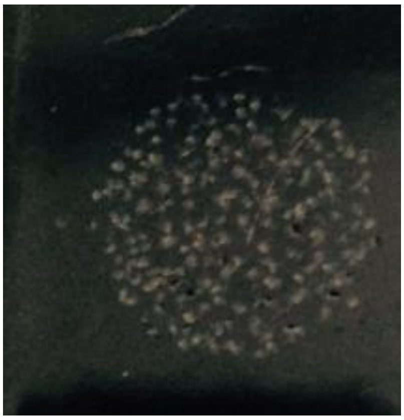


Figure 6: a) Permeation test performed by HELIOS II of ED specimen b) Photo of enamelled sample after test permeation.

Measurement of diffusible hydrogen content

Diffusible hydrogen content was measured by HELIOS III in specimens with enamel on both side, to quantify the hydrogen content that dissolves into the metal during enamel firing. In order to complete the degas process, samples were heated at 400°C for 1800s. As shown in figures 7-8 the results given by the instrument were reproducible for each couple of enamel-steel. Low diffusible hydrogen content in enamelled samples are in accordance with the low dew point temperature of furnace. In literature, dew point temperature of furnace is a parameter related with hydrogen content [12].

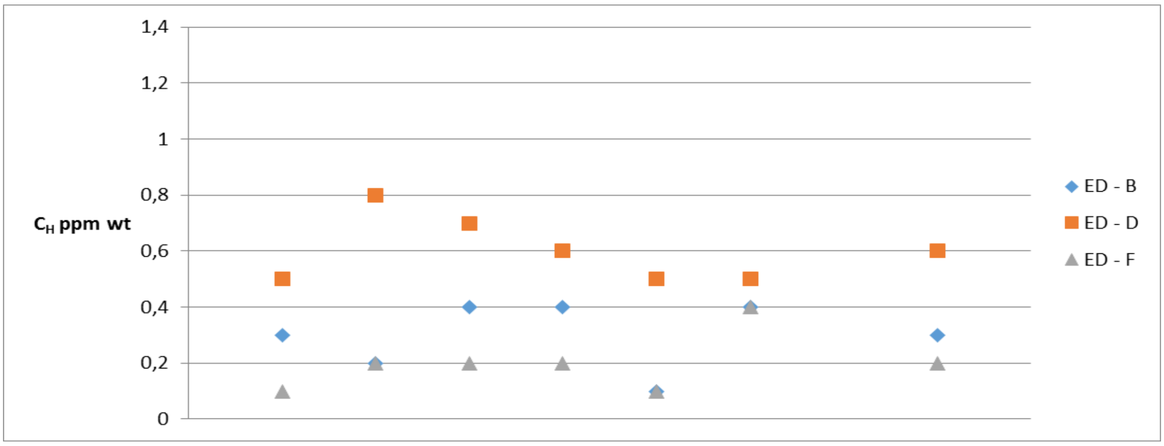


Figure 7: Diffusible Hydrogen Content in the ED enamelled samples..

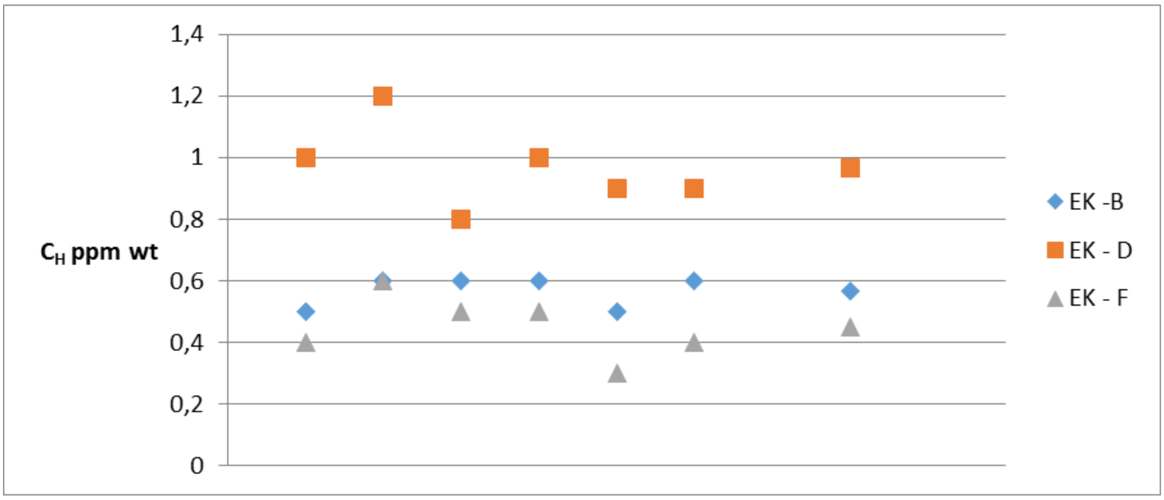


Figure 8: Diffusible Hydrogen Content in the EK enamelled samples

Conclusions

The present work established a series of important qualitative and quantitative results about the fishscale defect. The following evidences were observed:

1. It is possible to evaluate steel resistance to fishscale, using an innovative measuring procedure based on a recently developed device, that is easier than the procedure indicated by EN10029.
2. This evaluation produces quantitative results which can provide a comparative estimate of the materials and the technologies adopted in industrial enamelling processes.
3. This instrument can assess the enamel performance during forced fishscale by electrochemical test. In the examined conditions, the low diffusible hydrogen content in the steel, with enamel on both side, confirmed that fishscale defect depends on either the dew point temperature and the quality of steel. In fact, if the dew point temperature of the furnace is high, the hydrogen produced by the water in the air during cooking, which can produce negative effects on steel.
4. As the proposed methodology evaluates the enamel-steel interface, it can considered a base for the renewal of the standard. The presented results, even though statistically significant, are preliminary and a wider ranges of material and technological parameters should be investigated for completing the assessment of the fish scale phenomenon by the proposed methodology.

Acknowledgements and References

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