



The influence of cobalt on the microstructure and adherence characteristics of enamel on steel sheet

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Abstract

In this study, the influence of cobalt (Co) on the microstructure and adhesion between enamel and steel substrate has been investigated. The result of press test indicated that the adhesion strength was greatly improved by Co inclusion. Scanning electronic microscope (SEM) revealed that the amount of dendrite increases in the interface while its average size decreases. The wavelength dispersive X-ray analysis (WDS) identified the existence of Co in the dendrite, which confirms that the Co was closely related to the change of interface morphology and the improvement of adhesion strength. Finally, the reasons for adhesion improvement were discussed.

Keywords: enamel, cobalt, adhesion strength, interface

I. Introduction

Vitreous enamel is defined as a substantially vitreous or glassy inorganic coating bonded to a metal substrate by thermal fusion at temperatures above 800°C. Vitreous enamels represent smooth durable coatings with many excellent properties including abrasion, wear and chemical resistance, high hardness, brilliant colours and incombustibility. A tendency to crack or shatter when the substrate is stressed or bent is the main disadvantage of such coatings.

The enamelling procedure on a steel surface has been studied by many researches from various points of view [1–24]. To ensure good adherence of the enamel, different methods of pre-treatment of the steel sheets plates have been tested including pickling using dilute H₂SO₄ [1,2], high power diode laser surface treatment [3–6] and electrochemical processing [7].

In addition to common thermally induced fusion technology some other unconventional coating processes have been investigated such as plasma spraying [8], sol-gel methods and enamelling using electrophoresis. With the aim of modifying structure and composition of

the steel-enamel interface, doping of enamels with selected transition metal elements or pre-treatment of the steel surfaces with such elements has also been used. Most commonly used elements include Ni [1,7,9–16], Co [12,14] and Ti [11,13,14]. Doping of enamel with Co or pre-treatment of the steel surface with Co was observed to be more effective than procedures with Ni, Ti or that without any transition elements [14,17]. Transition-metal pre-treatment leads to more complex oxidation of the steel surface [16].

Many of the published works have focused on the phases formed on the steel-enamel interface. The study of the composition of the phase boundary between the vitreous and metallic phase is essential if a better understanding of the adhesion process and efficient corrosion protection is to be achieved. Until today, it has not been possible to completely describe the mechanism of enamel adherence. When simplifying matters greatly, there are, however, two model concepts which could be used for guidance:

(i) Chemical model: A continuous shift of the type of bond must be achieved in the region of the phase boundary from the metallic bond of the base metal via an oxide adherence layer to the ionic bond of the enamel layer.

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Table 1. The ingredient of ground-frit (wt.%)

	SiO ₂	B ₂ O ₃	Na ₂ O	K ₂ O	Li ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Co ₃ O ₄	MnO	NiO	F	CuO
CCE	56.44	14.9	14.36	0.51	0.99	3.06	3.1	-	2	1.12	1.5	1.63	0.39
FCE	56.2	14.8	14.2	0.5	0.5	3.3	-	6.6	-	-	2.5	1	0.4

(ii) Mechanical model: The prerequisite for good adherence is the roughening of the interface surface leading to a tight mechanical clinging of the enamel to the steel surface. Such roughening of surface is obtained when the attack on the iron in microscopic ranges is not uniform, but occurs as concentrated localized attack, if possible of the “pitting type”.

The main aims of the present study were to study the effect of cobalt additive on adherence strength of enamel to the steel substrate. The effect of additive on adherence strength was deeply investigated thoroughly by several researchers. However, the presented paper contains some prominent aspects that can not be found in the mentioned literature. First of all we have done adhesion test for investigation of effect of cobalt on metal-enamel interface. Secondly, although our study, like some works, studied cobalt in the enamel/steel interface through maps, the present paper is distinguished by the use of the Line-Scan method of characterisation. Moreover, in this study enamel was applied directly on the steel surface immediately after heat-pre-treatment and sandblasting. Meanwhile, in those works, the pre-treatment is based on the chemical preparation of the substrates. Thus, naturally, some metal oxide, which can be formed (especially nickel oxide), has direct influence on adhesion strength [17,25].

For investigating the adherence mechanisms, a method of microanalysis (in the nanometre-range), would be desirable. This can be fulfilled to a certain degree by Auger electron spectrometer (AES) investigations on micro-sections slightly inclined against the surface. In this work, however, we had at our disposal only our electron probe microanalyzer (ARL-SEM-Q with four wavelength-dispersive spectrometers and computer control) and had to be satisfied with the inherent resolution of the order of 1 µm. Electron microprobe analysis (EMPA) has been used for monitoring the various phases and explaining their formation mechanisms.

II. Experimental

2.1. Preparation of enamel specimen

The chemical compositions of the cobalt-free (FCE) and cobalt containing (CCE) frits used in this research are given in Table 1. The frit was prepared according to the following process: at first the raw materials were evenly blended and melted in a crucible at 1200–1280°C for 2 h, and then crushed and wet ground for 18–22 h. The obtained frit powder was finally filtered with 200 mesh screen and aged for 1–2 days.

Table 2. Analysis of steel before and after pre-treatment

Element	Content of elements [%]	
	Before treatment	After treatment
Fe	98.8591	98.9345
C	0.1340	0.0151
Si	0.0170	0.0281
S	0.0063	0.0065
P	0.0082	0.0083
Mn	0.8805	0.8866
Ni	0.0202	0.0216
Cr	0.0000	0.0000
Mo	0.0011	0.0015
V	0.0054	0.0059
Cu	0.0126	0.0157
W	0.0036	0.0053
Ti	0.0009	0.0012
Co	0.0080	0.0093
Al	0.0568	0.0677
Pb	0.0307	0.0293
B	0.0001	0.0001
Nb	0.0242	0.0259
Zr	0.0043	0.0070
Zn	0.0048	0.0065

Slabs (10×10×0.08 cm) of *st37 steel* were used as a substrate for enamelling. In order to avoid trouble in subsequent operations, it is essential that all traces of oils and greases are removed. Thus, samples are treated according to the following steps:

1. sand blasting,
2. annealing at 850°C in order to decarburization,
3. sand blasting.

Analysis of the steel before and after the pre-treatment is given in Table 2.

2.2. Adherence strength test

In accordance with EN10209 [17], the Europe standard test for the enamel adherence strength, the enamelling specimen is tested by the steel ball falling impact. Following the destruction, the adherence strength was judged according to the relics of enamel on the destroyed surface. The enamel adherence strength can be graded into 1st, 2nd, 3rd, 4th and 5th grade, where the 1st grade is the best.

Adhesion property was judged by the morphology of the remaining enamel layer on pressed concave

surface. The morphology and chemical composition of the intermediate bonding layer between enamel and the steel substrate were investigated by SEM and Line-Scan measurements, respectively.

III. Results and discussion

In investigating the validity of the previously described theory, it was desirable to learn whether galvanic corrosion could occur under the conditions encountered during the short firing periods used in applying

enamel to steel. To obtain such information several experiments were performed.

Figure 1 exhibits degree of coating degradation after the adhesion strength test. As it can be seen in Fig. 1b, most of the test surface is black and grey while only a few small regions are white. Adversely white area has occupied a great percent of surface in Fig. 1a while black area a much smaller portion of the image. Since the white colour refers to the peeled surface without enamel, and the black colour represents the unpeeled

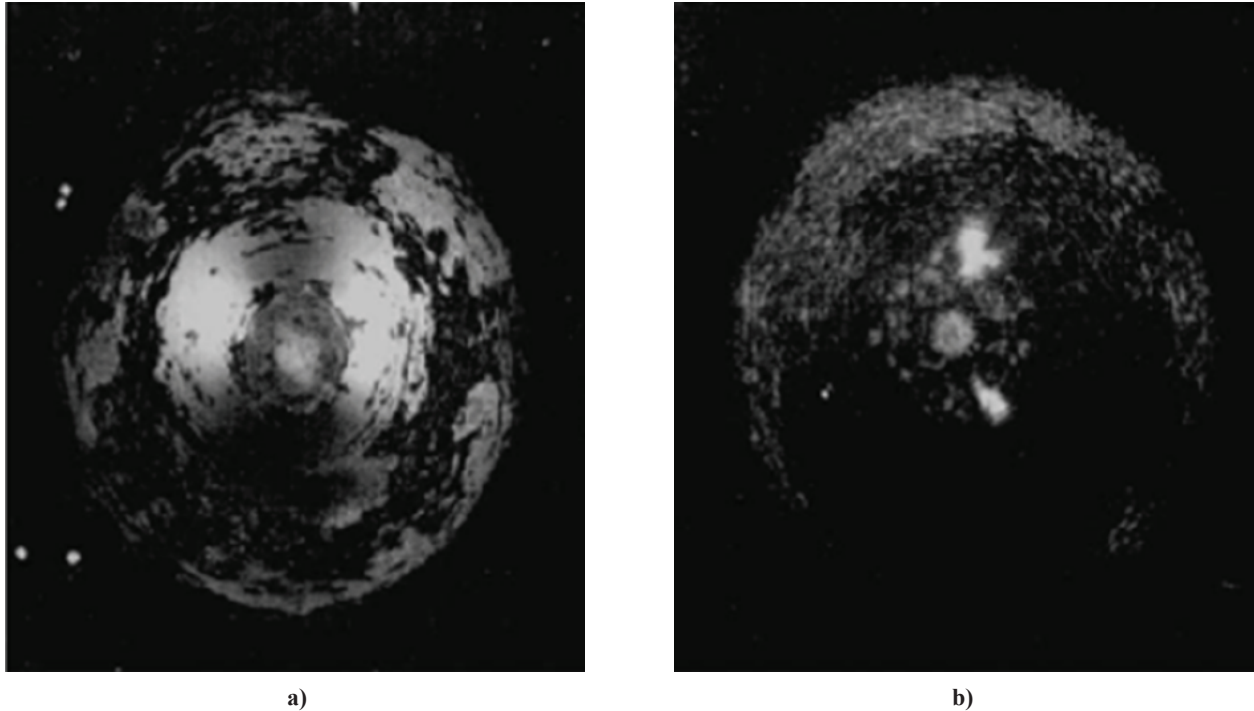


Figure 1. Photographs of peeling surface with press test of frit: a) without cobalt and b) containing cobalt

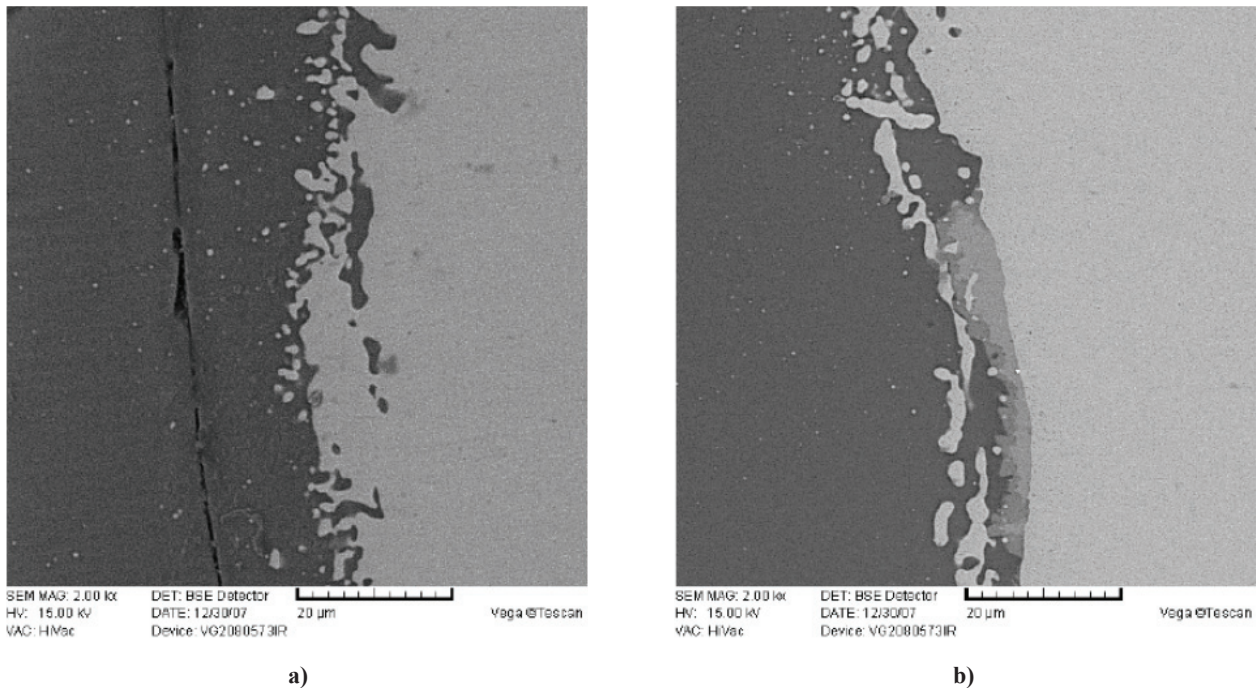


Figure 2. Cross-sectional BSE-images of the steel-enamel interface after the enamelling procedure: a) cobalt-free enamel and b) enamel with cobalt

surface with adhesive enamel layer, the enamel containing cobalt (Fig. 1b) demonstrates the fact that cobalt has a beneficial role in adhesion strength. Moreover, most of the cobalt-free enamel layer was removed from the steel sheet, and the surface appears silvery bright after the impact, thus, the adherence strength is poor and of 5th grade. Meanwhile most of the enamel layer remains on the steel sheet and the adherence strength of the enamel containing cobalt is excellent and of 1st grade.

So, under the same firing condition, the frit including cobalt displays the better adhesion strength to the steel substrate than the cobalt-free frit.

In order to analyse the interface between the frit containing cobalt and cobalt-free frit as coatings with mild steel sheet as the substrate, SEM images of the microstructure of the interface under the same firing conditions were recorded (see Fig. 2).

Figure 2 shows the cross section between coating and low-carbon content steel substrate. The main point of the images is the existence of a rugged boundary on the interface of enamel and steel substrate. In general galvanic corrosion reaction is the main cause of this [26]. However, the amount and size of the precipitated dendrite affects the adhesion within the interface in different way for the enamels with and without cobalt. Figures 2a and 2b are related to cobalt-free enamel and enamel including cobalt, respectively. As it is obvious, the amount of dendrite region is much higher in the enamel with cobalt than in the cobalt-free enamel. In other words, in the cobalt-free enamel, diffusion of glaze to substrate is too low for the reaction to promote adhesion. In contrast, in Fig. 2b, a distinctive narrow region placed in the substrate proves that enamel has a much higher tendency for

reacting with the substrate and confirms how adhesion is improved with the inclusion of cobalt.

In order to understand the role of cobalt in improving the adhesion strength, in Fig. 3 galvanic corrosion has been represented schematically. It shows a sequence of highly magnified interfaces between iron and two enamels at three stages of a normal firing period. Figures 3a and 3b typically simulate behaviour of enamel in the interface without and with cobalt, respectively. Figure 3a illustrates the changes in interface with firing time for the cobalt-free enamel. Figure 3b exhibits how a small amount of cobalt oxide in enamel changes corrosive treatment. As was already mentioned in the experimental part, for the schematic drawings the surface of low-carbon content steel is assumed to be polished flat before enamelling.

Figure 3a₁ represents the condition of the interface shortly after the coating has dissolved the oxide layer, i.e., quite early in the firing cycle. Of course, there will be some oxidation of iron before the enamel fuses, but in the schematic drawing the interface is considered at the stage just following the time when the oxide layer is first dissolved. Figure 3a₂ represents the condition of the interface a minute or two later and the third picture, Fig. 3a₃, represents the interface after a normal firing of 4 to 6 minutes. The distance from the interface to the reference line, drawn in the figure as an extension of the interface line shown in Fig. 3a₁, represents the depth of corrosion at any location. The drawing, which was made after numerous observations of sections under the electron microscope, shows that the iron is being corroded, but that it is being corroded uniformly.

The corrosion of iron when cobalt ions are present in the enamel layer is completely different. When the

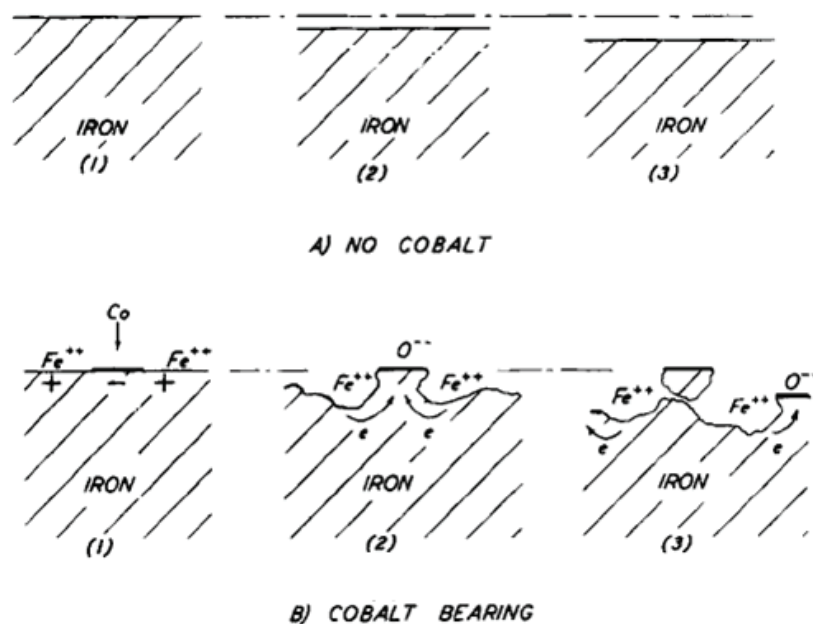


Figure 3. Schematic drawing illustrating the differences in the corrosive attack to iron by cobalt-free and cobalt-bearing ground coats. The firing time increases in both sets of diagrams from left to right, the first diagram in each case indicating the interface condition shortly after the enamel fuses

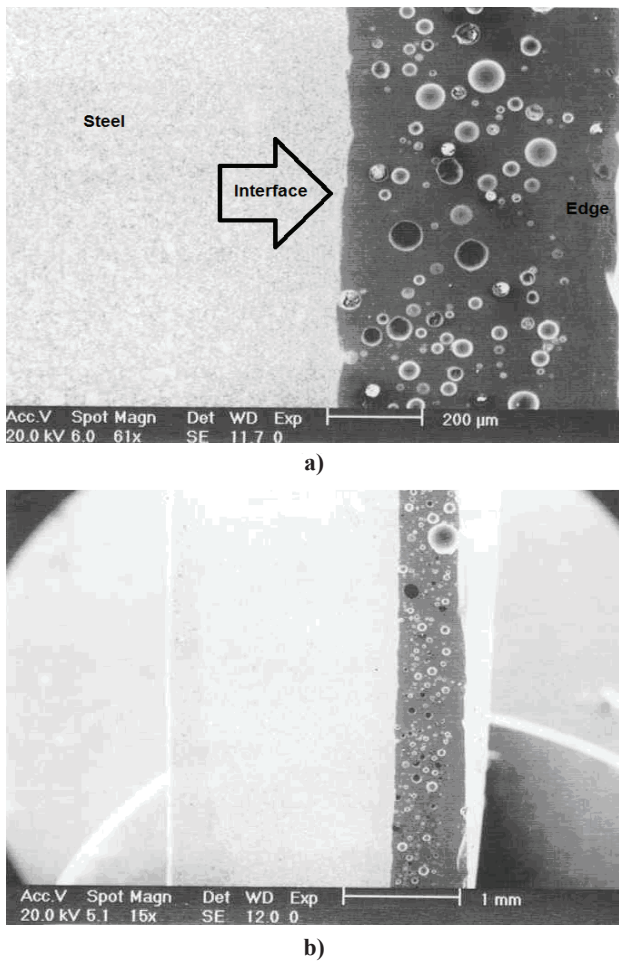


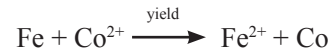
Figure 4. Typical tapered cross-section SEM images in sample with content cobalt (a) high magnification of the interfacial region showing the presence of Fe metal-rich dendrites at the base of bubbles and (b) low magnification image showing the presence of large bubbles at the interface

enamel fuses, it first wets the oxide layer that is formed on the iron during the heat-up, i.e., while the initially cold specimen is approaching furnace temperature. As soon as the oxide layer is dissolved, cobalt from the ground coat begins to plate out on the cathodic areas of the iron surface. This is shown schematically in Fig. 3b₁. Patrick *et al.* [27] demonstrated that metallic cobalt is deposited on iron during normal firing by the radioactive tracer work and X-ray spectrographic study. In line with the galvanic corrosion theory the cobalt first plates out on the cathodic areas of the iron surface. There are as many as ten different factors that will produce potential on a metal surface immersed in an electrolyte. The molten ground-coat enamel is an electrolyte having conductivity at the firing temperature estimated to be of the same order of magnitude as that of a molten glass high in alkali or about 0.20 mho*. It is logical to believe that

*Defining "mho" - The SI derived unit of electrical conductance, equal to one ampere per volt. It is equivalent to the reciprocal of the ohm unit.

potential differences could exist on the iron surface covered with enamel from such factors as the grain boundaries being anodic with respect to grain interiors, or one metal grain at the surface being anodic with respect to an adjacent grain with a different orientation.

Assuming that such potential differences do exist, cobalt will first plate out on the cathodic areas. The plating reaction might be written as:



One such area is shown schematically in Fig. 3b₁. The instant the cobalt makes electrical contact with the iron a tiny galvanic cell is formed in which the iron acts as the anode and the cobalt plated area as the cathode.

In this picture, iron is going into the molten enamel as Fe²⁺ ions and electrons are given up in the process. These flow to the cobalt-plated area where they create a reducing condition. Any atmospheric oxygen dissolved in the glass could pick up these electrons and become O²⁻ ions, and consequently any easily reduced metallic oxides, or even the dissolved water in the glass for that matter, would tend to be reduced, thus introducing more O²⁻ ions into the coating. For the galvanic cell to function, there would need to be the same number of O²⁻ ions formed at the cathode as there are Fe²⁺ ions at the anode. Therefore, if the supply of oxygen at the cathode should be shut off for any reason, the flow of electrons could not continue and the corrosion process would come to a stop. The galvanic cell action would, of course, produce a preferential attack on the iron surface. This is shown schematically in Fig. 3b₂. It is easy to visualize that the cathodic areas as illustrated in Fig. 3b₂ would provide anchor points to key the coating to the metal. Corrosion would be proceeding rapidly, however, and the stage shown in Fig. 3b₂ would change with firing time to the stage shown in Fig. 3b₃, in which continued corrosion has caused a fragment of the steel to become detached.

As is well known, dendrite is formed from the melted enamel during the cooling process through nucleation and growth stages. According to the thermodynamic principle, the dendrite solidification is a heterogeneous nucleation process and these nucleuses usually occur on the surface of the steel substrate, which is the reason why the dendrite exists as part of steel substrate [18–20]. In the case where the gas bubbles exist within the interface, the nucleation readily occurs on the surface of the gas bubbles [19]. If solid particles exist in the glass phase, the nucleation will reverently take place on the surface of the solid particle. Other factor in adherence is bubble structure and distribution.

Bubble structure and its effect on fish scale resistance have already been investigated. The benefits of developing bubbles at enamel steel interface where described. The main cause of fish scaling lies in the difference of the coefficients of expansion of the enamel

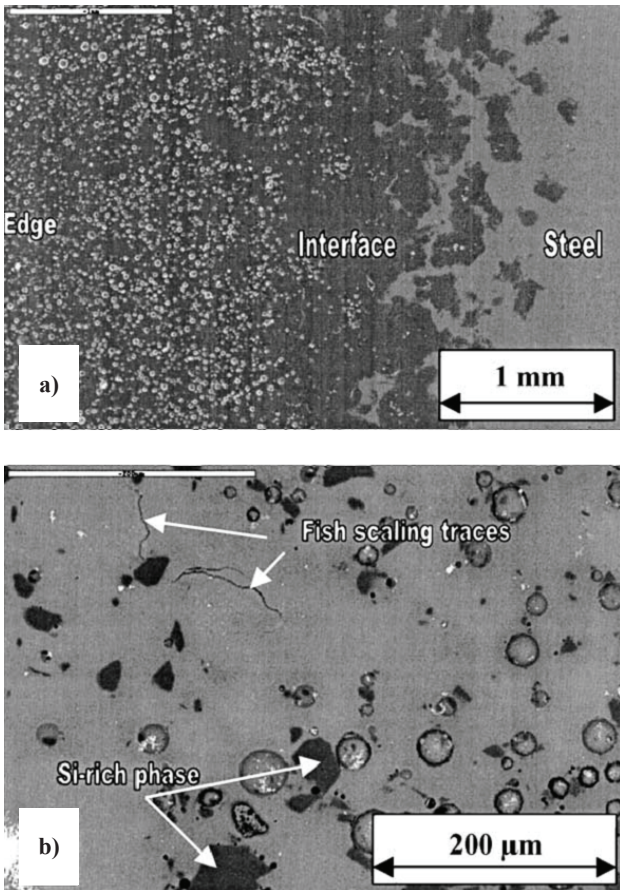


Figure 5. Typical tapered cross-section SEM images in sample without cobalt (a) low magnification image showing the absence of large bubbles at the interface and (b) high magnification image of the interfacial region showing traces of fish-scaling and the absence of Fe metal-rich dendrites at the base of bubbles

and the stock, which is higher for steel than for enamels so that the latter are under a compressive stress. One of the effective ways of changing the thermal expansion coefficient of the enamel is to incorporate metal oxide in its composition. Transient metal oxides especially nickel oxide and cobalt oxide can change the amount of fish scaling and bubble size in the interface of steel and enamel. These positive effects have been reproduced and observed. As shown in Figs. 4 and 5, the amount of bubble size and its distribution at the interface depends on presence of cobalt oxide. SEM Images of the enamel containing cobalt (Fig. 4) taken at two different magnifications are compared to those of the enamel without oxide cobalt (Fig. 5) and prove that the rising tendency to fish scaling and distribution of smaller bubbles is strongly dependant on the cobalt oxide. In the cobalt-free enamel, due to the closed bubbles a certain amount of hydrogen remains free in the ferrite matrix, and is the most responsible for fish scaling. On the other hand, cobalt oxide is responsible for producing the sponge-like structure of iron which provides an escape rout for the hydrogen through this reaction (Figs. 4 and 6). Therefore the probability of fish scaling is reduced by changing in enamel composition i.e. by adding cobalt oxide.

For investigating adherence mechanisms, a method of microanalysis (in nanometre-range), would be desirable. This can be fulfilled to a certain degree by Auger electron spectrometer (AES) investigations on microsections slightly inclined against the surface. In this work, however, we had at our disposal only our electron probe microanalyser (ARL-SEM-Q with four wavelength-dispersive spectrometers and computer control) and had to be satisfied with the inherent resolution of the order of 1 μm.

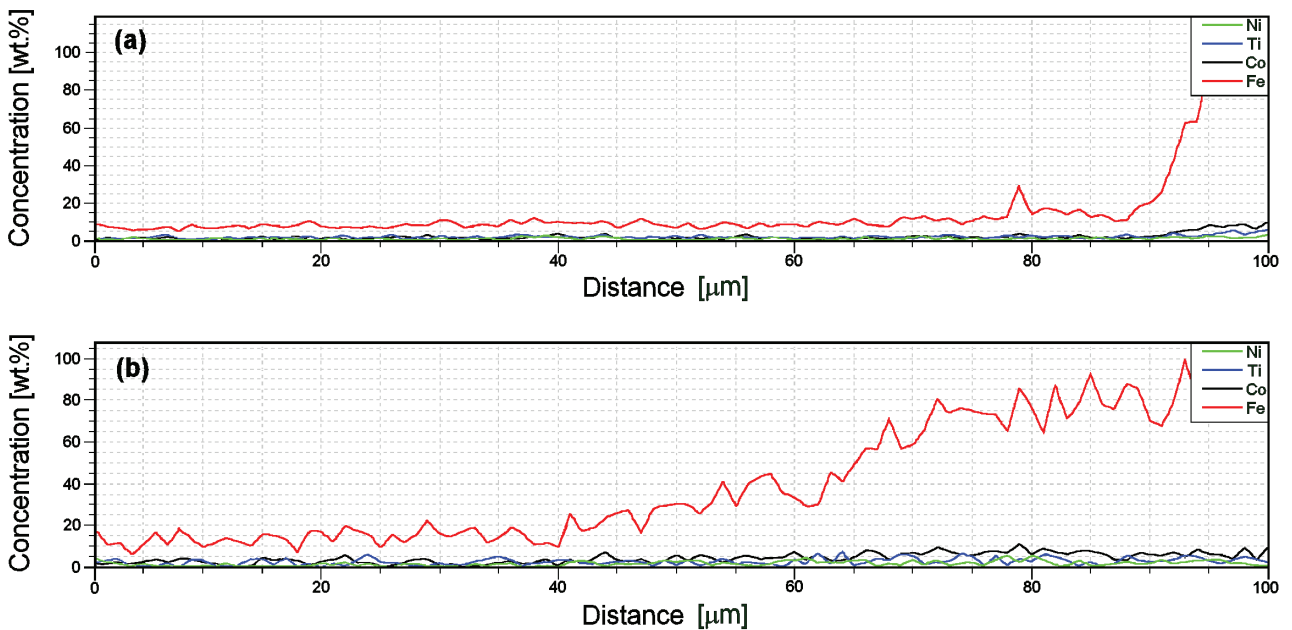


Figure 6. Diffusion of iron from the steel into the enamel mesured by Line-Scan: a) cobalt-free enamel and b) enamel containg cobalt

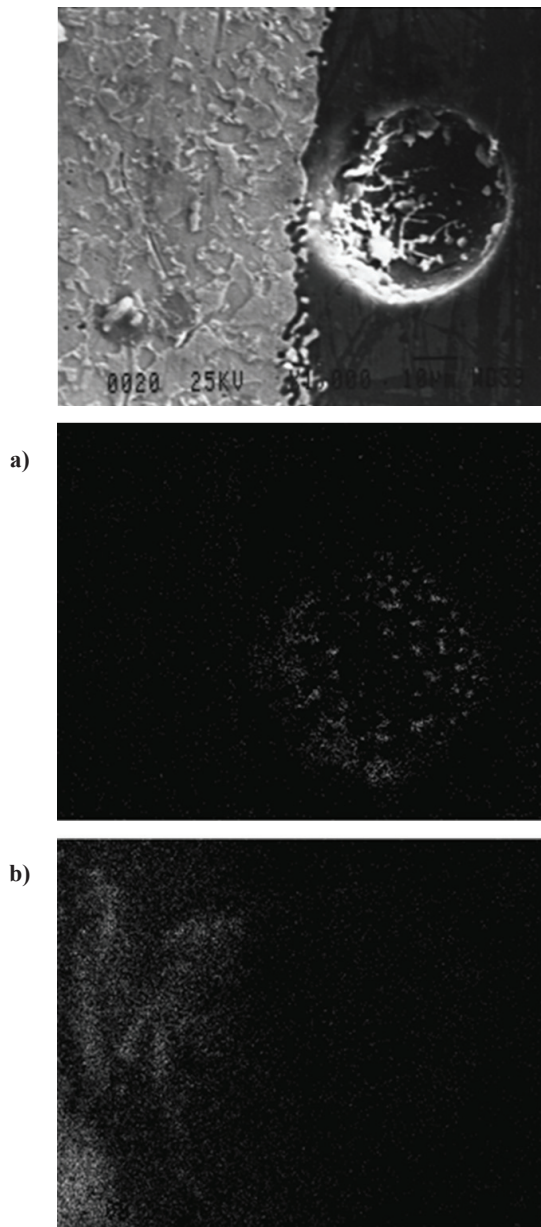


Figure 7. X-ray maps of sample with cobalt: a) Fe and b) Co

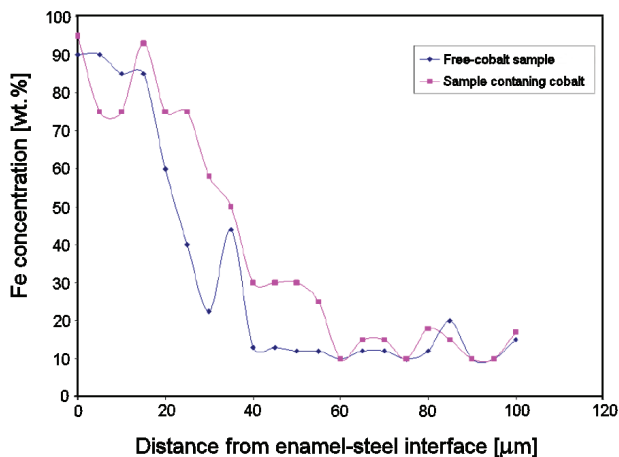


Figure 8. Diffusion profile of Fe element within the enamel layer of samples without and with cobalt

The structure and phase composition of the steel-enamel interface formed as a result of the reaction between melted enamel and the steel substrate were analyzed by Line-Scan. Atomic concentration distributions of Fe in the glass coating and the substrate of the specimen were analyzed by electron probe X-ray micro analyzer (Line-Scan). The sinter processing results in the enamel and substrate diffusing into each other and creating the transient layer in which the Fe, Co elements from the substrate exist, this is helpful for the glass coating to combine with the substrate closely. The glass based coating is homogeneous, and there are no such defects as grain boundaries and phase boundaries, which would allow carbon diffusion (see Fig. 4).

For the further investigation of diffusion of Fe and the effect of Co on the rate of diffusion the X-ray map analysis is performed. Figure 7 shows the map of the sample with cobalt. As it is shown, the diffusion of Fe to enamel and galvanic corrosion is absolutely obvious.

Figure 6 compares the concentration profile of Fe measured using the line scan in two types of samples. It can be seen that in spite of a rapid decrease in the concentrations of Fe with distance away from the glass-to-steel interface in both cases, the concentration of Fe present in the enamel content co material is much higher than in the enamel without cobalt, especially in the first 50 μm of enamel thickness. In the Line-Scan results, the analyzed iron represents FeO since in the presence of iron, the higher oxides of iron (Fe_2O_3 and Fe_3O_4) are unstable at temperatures above 540°C and will decompose and form FeO [28]. In addition, concentration profile of Fe element is shown in Fig. 8 for both samples without and with cobalt. It is obvious that diffusion of iron in enamel containing cobalt is more pronounced than in cobalt-free enamel.

IV. Conclusions

This work investigated the influence of cobalt on the adhesion of the glaze to the metal. The results showed that the composition of the enamel, i.e. cobalt content, plays a great role in the adhesion strength for both substrate and coating. The inclusion of cobalt greatly improved the adherence index for specimens heat treated for a few minute. On the other hand, without the cobalt adherence of the enamel to the steel substrate decreases and the firing time has to be increased. Moreover, the presence of cobalt as an element in enamel composition is effective in reducing fish scaling in contrast to cobalt-free enamel. The results of the investigation also proved that cobalt results in an appropriate surface roughening during the firing operation. Therefore a relationship was noted between the degree of roughening and the measured adherence index. In addition to these results, we confirmed that the galvanic corrosion can be effected by the cobalt anions meaning that the functionality of the cobalt in promoting adherence is believed to be associated with galvanic attack. The cobalt appar-

ently deposits from an aqueous solution selectively on more cathodic areas of steel surfaces, thus forming local galvanic cell which starts to function immediately after the enamel melts and wets the metal surfaces.

Overall, under most conditions the cobalt inclusion produced a rising trend in adherence index compared to the cobalt-free frit.

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