

Effect of thermal treatment on the property of enamel coating on steel substrate

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Abstract

This study concerned the effect of heat treatment on the vitreous enamel and the interface steel–enamel during firing. Color change was evaluated by comparing the color of the enamel steel after firing in different temperature. The thermal transformation of vitreous coating on steel was observed “in situ” with Infrared spectroscopy and X ray diffraction (XRD), the mechanical properties of the steel–enamel interface were also studied by using a nano-indenter. The interface reactions and the resulting structure can strongly influence the adhesion mechanism between glass coatings and the metal substrate. An in-depth investigation and structural characterization was therefore performed to define the correlation between interface morphology and the final chemical and mechanical properties of the enamel–steel interface.

1. Introduction

Enameling of steel surfaces has been done for many years on different types of steel, depending on the final application of the enameled pieces. Usually, enamel is a substantially vitreous or glassy inorganic coating bonded to a metal substrate by thermal fusion. It has many excellent properties including abrasion, wear and chemical resistance, high harness, brilliant colors and incombustibility.

The enameling procedure on a steel surface has been studied by many researches from various points of view [1-5]. The physical–chemical reactions occurring at the interphase enamel/metal guarantee a strong adherence between the two materials thus providing the enamel/metal system with good mechanical properties and excellent corrosion resistance [6-7]. Moreover, this coating presents many other advantages such as weathering and chemical resistance, resistance to high temperatures and fire, impermeability to liquids, due to its vitreous nature and the microstructure characterized by closed porosity. Several factors could affect interface reactions and the adhesion mechanism between the glass coatings and the metal substrate such as chemical composition of enamel, the type of steel, the roughness of the metal surface, the heating process and the temperature of glazing [1,7,8].

In the enamelling of the steel, it is generally considered that the oxide layer formed in the initial stages was completely dissolved by the molten glass, with the steel–glass bond formed directly between an oxide-saturated glass and the steel substrate [9]. However, some researchers have also presented the evidence for the presence of a layer of wustite at the enamel–steel interface [10] and [11]. The presence of such a layer may indicate that the glass–steel bond is dependent on oxide–metal adherence. As most conclusions to date are based on optical microscopy and chemical analysis, a transmission electron microscopy (TEM) investigation of the type, distribution and morphology of any oxides present at the enamel–steel interface, is also necessary to verify existing adherence models.

Although many papers have been published on this topic, the base mechanism related to the metal–enamel interface formation during firing is not still clear and needs further and in-depth investigation [12,13]. The aim of the present study is to analyze "in situ" the melting process of the enamel by using X-ray diffraction and infrared spectroscopy and to obtain the mechanical properties of the steel-enamel interface by using a nano-indenter. Quantitative correlation between the structure of the interface and its chemical and mechanical properties was analyzed. This study was designed to evaluate the effect of heat treatment on the microstructure, properties, surface profile and color stability.

Table 1: The temperatures of firing and weight percentages of elements of enamels E1, E2 and E3.

Enamel	T _f	Si	Na	O	Zn	Al	K	Sn	Ti	Cr	Co	Mg
E1	840	24.07	6.43	54.08	1.99	1.92	1.77	3.58	1.70	0.38	—	3.21
E2	790	20.82	1.16	54.97	0.59	4.21	2.38	—	6.24	—	—	2.16
E3	750	15.07	5.10	49.42	1.87	2.07	—	18.45	0.78	—	5.91	2.20

2. Experimental details

2.1. Preparation of enamel

Enamels are typically silicate-based oxides that are deposited from slurries and fused at high temperature. The enamel slurry is prepared by milling glass frits, clay and certain electrolytes, then mixing with water to provide a stable suspension. Three types of enamels were investigated in this study. The ground coat (E1) is applied to the steel sheet to promote adhesion of the cover coat. Ground-coat frits contain oxides that help to promote adhesion between the steel surface and the enamel coating. The cover-coat enamel (E2) is applied over the ground coat. The double enamel was introduced to combine the superior corrosion performance of pure enamel and the better bond behavior of mixed enamel. It consisted of an inner pure enamel layer and an outer mixed enamel layer to increase its corrosion resistance through the inner layer and enhance its bond strength through the outer layer. Finally Enamel of decor (E3) is durable, gloss synthetic coatings for protection of steel. They have been specifically developed for protection and decoration of metal exposed to industrial application. The enamels are fired at the temperatures of between 750°C and 850°C. The firing temperature depend the steel and the type of enamel. Good adhesion is produced by reaction and fusion of the porcelain enamel coating with the base metal at relatively high temperatures that may fall within 750°C to 900°C ranges. The heating process, which promotes the bond creation between steel and enamel, was performed in an classical furnace. The firing time was 4 min, the samples was then cooled in air. The firing treatment melted the glass frit and chemically bonded the enamel to the steel substrate

The temperatures of firing and chemical composition of the three enamels were determined and is given in Table 1. The study focuses mainly on the effects of temperature of treatment on the microstructure and properties of the enamel (E3) and evaluating E2/E3 interface adherence.

2.2. Thermal treatment

In order to investigate the effect thermal treatment on microstructure and hardness of the vitreous enamel coatings on the steel substrate and the adhesion of the enamel to the steel substrate, the enameled specimens were held in a resistance furnace at different temperatures from 700 to 850 °C for 4 min.

2.3. Characterization of enamel coatings

The phase composition and microstructure of the enamel coatings were investigated with X-ray diffraction D8 Advance Bruker Bragg-Brentano diffractometer (Cu K_α radiation) equipped with a Vantec-1 linear detector. The microstructure of the enamel/enamel and enamel/steel interface on the cross-selection was examined using scanning electron microscopy (SEM) with an energy dispersive X-ray facility (EDX). For SEM measurements, 1.0-cm-long longitudinal cross sections were cut, cold-mounted and hand-polished with silicon carbide papers with grits of 80, 180, 320, 600, 800, and 1200. The samples were rinsed with deionized water, cleansed with acetone, and finally dried in air at room temperature. To avoid any potential disturbance of other elements, a carbon coating was applied during the SEM preparation.

2.4. Microhardness measurement

The hardness of the specimens was measured by using a Vickers hardness indenter. Specimens were prepared using conventional metallographic techniques, and the hardness tests were performed under an indentation load

of 500 g for 15 s. In order to obtain reliable statistical data, analysis points were spaced so as to eliminate the effect of neighboring indentations, and the hardness was evaluated by taking ten indentations on each specimen and averaging of only five middle values. The Vickers hardness values (in GPa) were calculated from the following equation:

$$HV = \frac{1.8544P}{(d)^2} \quad (1)$$

where P is the applied load and d is the average length of the two diagonals. The eyepiece on the microscope of the equipment allowed measurements with an estimated accuracy of 0.5 μm for the indentation diagonals.

3. Results and discussion

3.1. Visual Observations

Representative micrographs of the enamel steel surface after firing at different temperatures are presented in Fig. 1. Optical microscopy under reflective light indicates that the quality of color changes according to the cooking temperature. These photos show the presence of microparticles distributed in the surface of the samples. The concentration, the size and the aggregation of microparticles formed are strongly affected by the temperature the firing. The firing temperature could be one of the major reasons for the color stability.

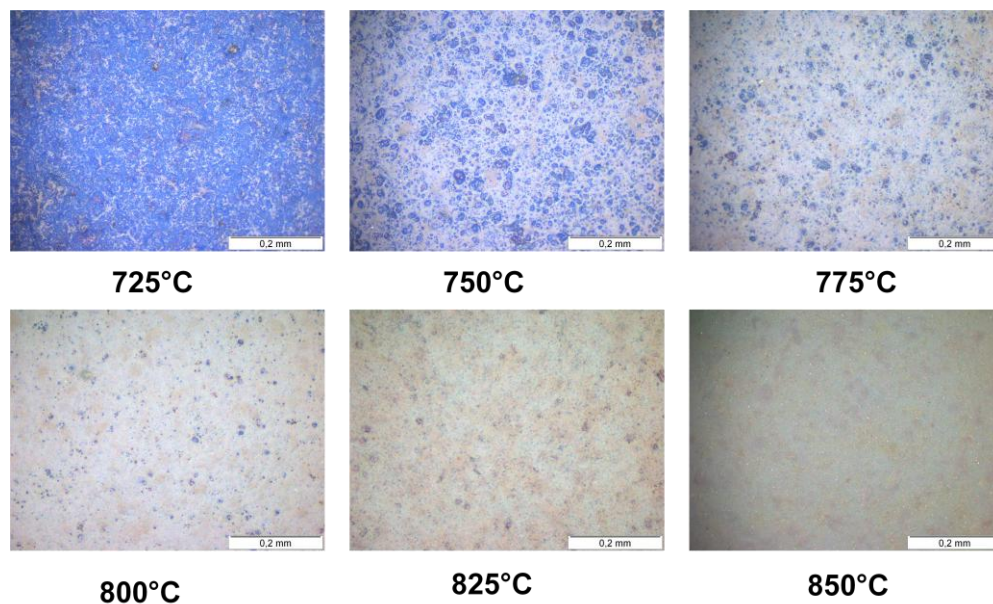


Figure 1: Optical micrographs of the enamel steel surface after firing at different temperatures.

3.2. XRD measurements

The main goal of this investigation was to analyze the modification of structure cristallines of the enamel bleu during de firing. Figure 2 shows the XRD patterns of the enamel steel after firing at various temperatures. As shown in the result of XRD, It can be clearly seen that the enamel after firing at 700 °C mainly consists the diffraction peaks of SnO_4 and Al_2CoO_4 crystals. When the temperature of firing increases, the main diffraction peaks of the cristobalite phase appear and their intensities are increase with temperature. When the temperature of firing gets higher than 750°C, the intensities of diffraction peaks of Al_2CoO_4 and cristobalite decrease and disappear totally after the firing in 825°C. Therefore, the diffraction peaks of the Mg_2TiO_2 and $\text{Co}(\text{TiO}_3)$ phase appear after firing in 825°C, indicating an transformation of phases of the enamel during the treatment. Formation of new phases resulting from chemical reactions at metal-ceramic interfaces for enhancing the bonding strength [13]. In order to investigate the relationship between the microstructure and temperature of firing, the powder enamel were put into furnace and reheated from room temperature to elevated temperature and holding at different temperatures for one minute. Fig. 3 shows in situ high-temperature XRD patterns of the enamel mixed with the pigment. Data were collected at the temperatures between 100 and 850 °C. The temperature pattern is similar at the temperatures between 100°C and 300°C. However, we observe that a temperature increase of 400°C, is sufficient to the cristobalite forming and his quantity increase with temperature. By further heating above 690°C, the cristobalite appears, indicating a new phase transition is observed towards another phase which was observed in previous study [14].

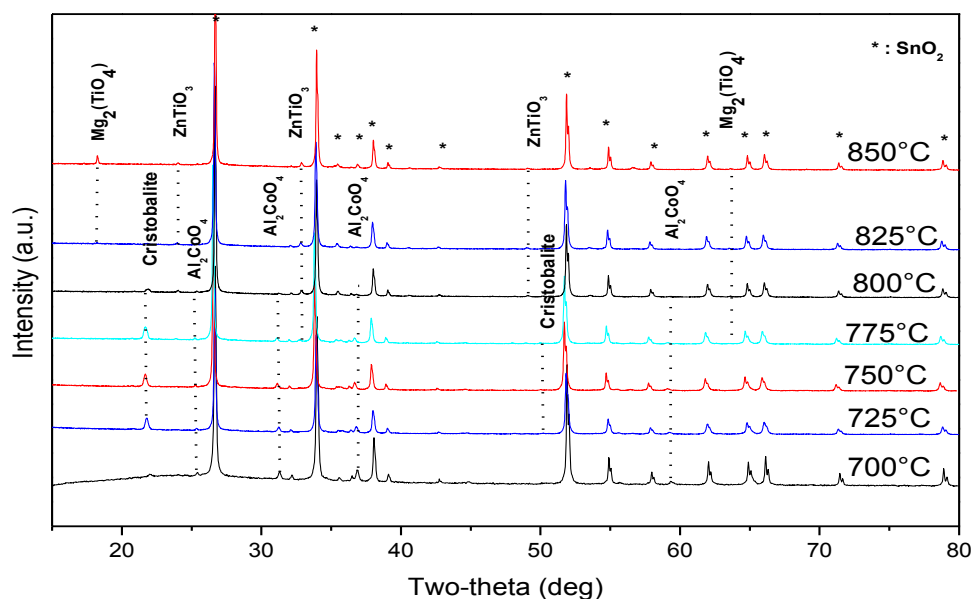


Figure 2: XRD patterns of the enamels heat treated at different temperatures.

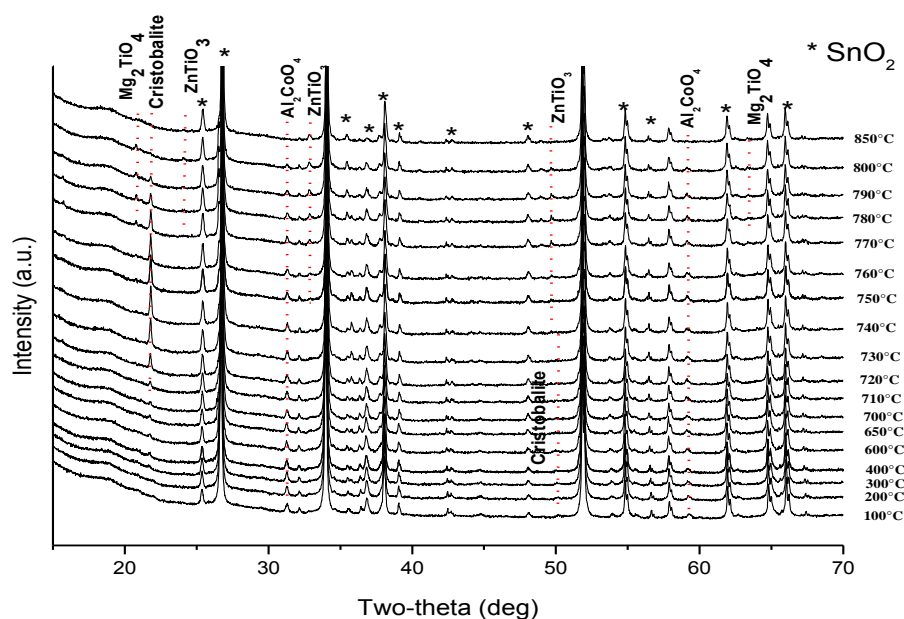


Figure 3: High-temperature X-ray diffraction patterns of enamel steel.

3.3. FTIR analysis

In order to complement the information provided by X-ray diffraction analysis. The characterization of the steel surface was carried out by infrared spectroscopy at different temperatures. The reflectivity spectra of the layer deposited on the steel surface is shown in Fig. 4. Of particular interest are the systematic changes in the shape and position of the primary Si–O–Si (stretching mode). Asymmetric stretching motions of Si–O bonds inside tetrahedral entities are located within the 850–1200 cm^{-1} region of the spectrum [15]. Going deeper in the attribution, the high frequency part of this domain above 1040 cm^{-1} is due to components involving bridging oxygen (BO). The one originating from Q^4 SiO₄ tetrahedral for which all the four oxygen atoms are bridging oxygen appear around 1050 cm^{-1} [15]. When the temperature of firing was better than 725°C, we can observe the appearance of two absorption bands near 1055 cm^{-1} and 800 cm^{-1} . The appearance of these absorption bands due to the symmetric stretching vibration of cristobalite [16-19]. The intensities of these absorption bands increased with the increased temperature, which indicates that the trend of cristobalite phase formation increased gradually. When the temperature of firing increased to 825°C these bands disappear. We studied the enamel steel by in-situ-FTIR spectroscopy as a function of temperature. The heating was provided by heating a

ceramic plate mounted in contact with the rear facet of the sample. Figure 5 compares the measured reflectivity spectra of enamel steel for different time intervals.

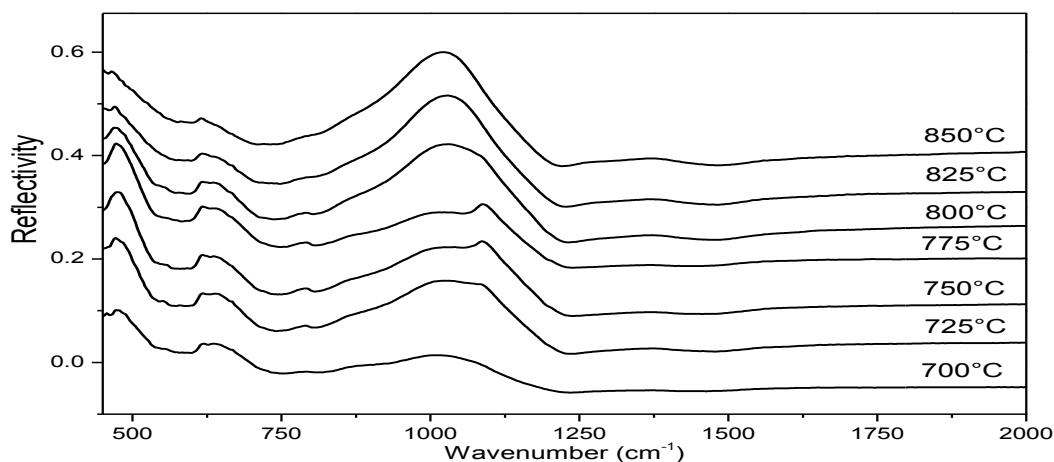


Figure 4: Fourier transform infrared absorption spectra of enamel steel.

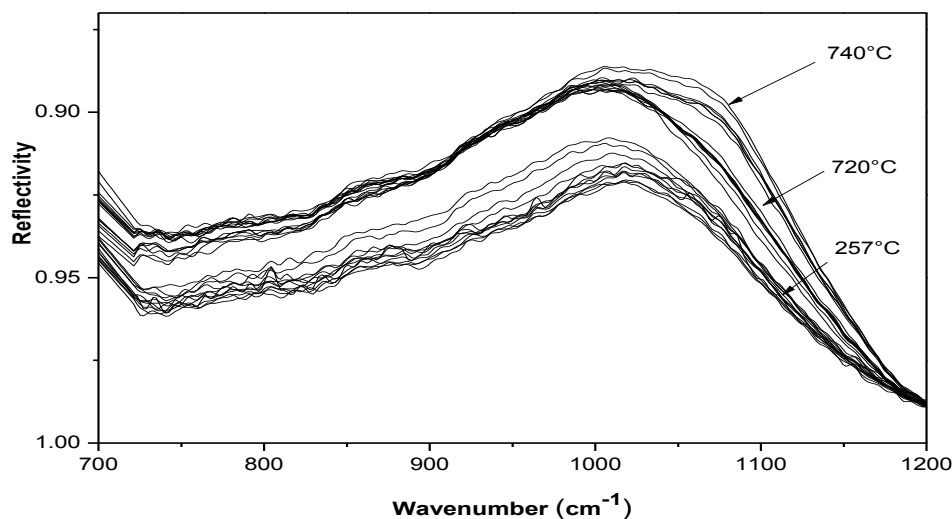


Figure 5: Spectra of experimental reflectance enameled steel depending on the temperature.

With temperature increase, change in the functional groups takes place forming numerous intermediate species. At low temperature, the spectra stay similar, when the temperature increases (between 250°C and 700°C), the intensity of the band at 1000 cm⁻¹ was increasing exhibit small change structural inside the sample. When the temperature was ramped up 750 °C, the reflectance spectra are more complex and present band broadening due to the appearance of cristobalite stretching mode [20]. This confirms the result obtained previously. Based on X-ray diffraction and TR spectra analysis, the temperature of firing did influence on the enamel steel network. As already reported by Barcova et al. [21], these crystalline phases are formed during heating because an intensive thermal effect induces an oxidation process on the enamel surface.

3.4. Surface, cross-sectional and enamel-steel interfacial morphologies

The specific metal-enamel interface forms during firing of enamel on steel sheet surface and its properties could be significantly influenced by the pre-treatment of this surface. Because surface/interface morphology plays an important role for quality of color, the steel sheets were studied using the scattering scanning electron microscopy and chemical composition using energy dispersive X-ray microanalysis before and after firing in the furnace. Figure 6 shows longitudinal cross sectional SEM images of the three types of enamel coatings adhered to steel. It can be clearly observed that the surface and cross-sectional morphologies of the three enamel coatings are quite different. As shown in Fig. 6, the ground enamel coating is approximately 150 μm thick. The enamel coating has air bubbles that were formed during the firing process as a normal part of the enameling process.

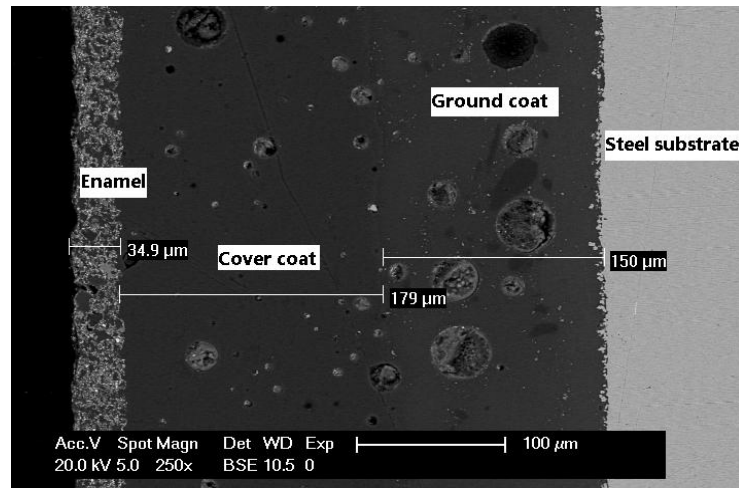


Figure 6: Cross-sectional SEM micrograph of enamel/steel interface.

These air bubbles were formed from gases such as CO_2 , CO , H_2O and H_2 that result from high temperature chemical reactions between the carbon, iron and other elements in the steel and the water and oxides in the enamel frits [1]. The cover enamel coating is $180\ \mu\text{m}$ thick, and has a few bubbles as shown in Fig. 6. As illustrated in fig, the enamel decor ($35\ \mu\text{m}$ thick) has no air bubbles. The porosity remains confined in the thickness of the layer and it is absent on the enamel decor, which appears very smooth. This aspect, typical of vitreous enamel coatings, guarantees good corrosion properties of this kind of deposits [22].

The specific metal-enamel interface forms during firing of enamel on steel sheet surface and its properties could be significantly influenced by the pre-treatment of this surface. Fig. 7 shows the SEM images of the surface and cross-sectional views of the enamel coating after firing. It can be clearly observed that the surface and cross-sectional morphologies of the enamel coating are quite different.

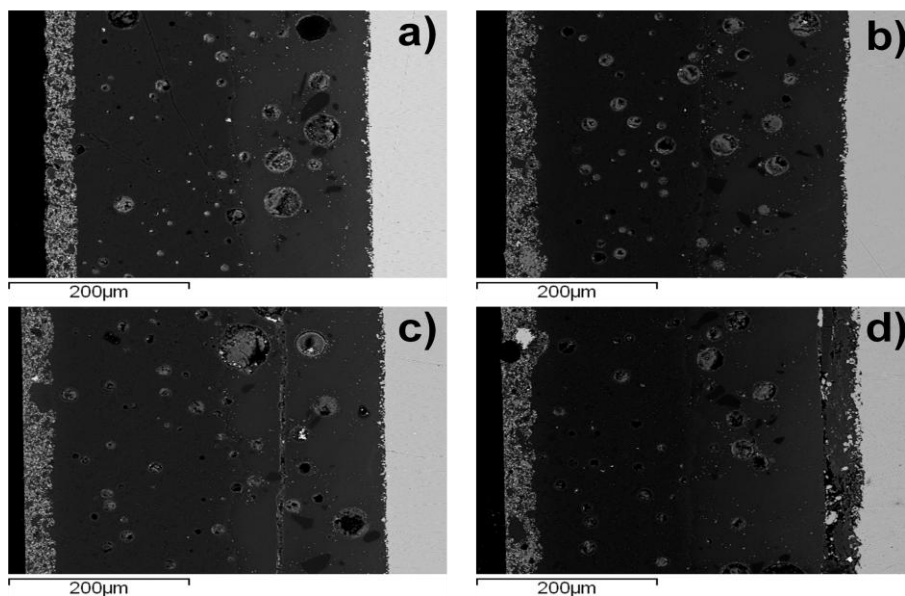


Figure 7: Effect of temperature treatment on the morphologies of enamel/steel: (a: 700°C ; b: 750°C ; c: 800°C and d: 850°C).

After the treatment at 700°C , the enamel/steel interface (Fig. 7a) has basically the same roughness as the original surface of the pretreated steel substrate. The periodicity of the interface wave remains nearly unchanged. The sample treated at the temperature 750°C , small islands of black spots are present at the enamel/steel interface, which indicates the formation of the so-called anchor points (Fig. 7b). Further increase in temperature ($T = 800^\circ\text{C}$) results in the occurrence and exuberant growth of the steel/enamel interface (Fig. 7c). A typical micrograph of the enamel–steel interface is shown in Fig. 7d ($T = 850^\circ\text{C}$). This figure shows small islands in the interfacial region, it can be noted that the islands form the so-called anchor points; thus the roughness of steel in the interface is increased [23,24].

The concentration profiles of the main elements were determined with line scans by EDX between the enamels and the steel. Figure 8 compares the concentration profile of Co measured using the line scan of the enamel steel after firing at various temperatures. As it can be seen in the figure, the concentration profiles of the cobalt between enamels (E1, E2 and E3) and the steel are radically different after the treatment at different temperatures. By EDX analysis (Fig. 8), Co enrichment is found on the enamel decore (E3) substrate. It can be observed that the temperature of firing has a significant influence on the diffusion of cobalt between the enamels and the steel. After firing in high temperature (850°C), the cobalt, diffuses from the enamel decore (E3) to cover-coat enamel (E2), could promote the change of quality of color. It is obvious, that the partial thermally induced reduction was probably caused by the transition metals (Zn, Ti, Co, ...) in coloring pigments [1].

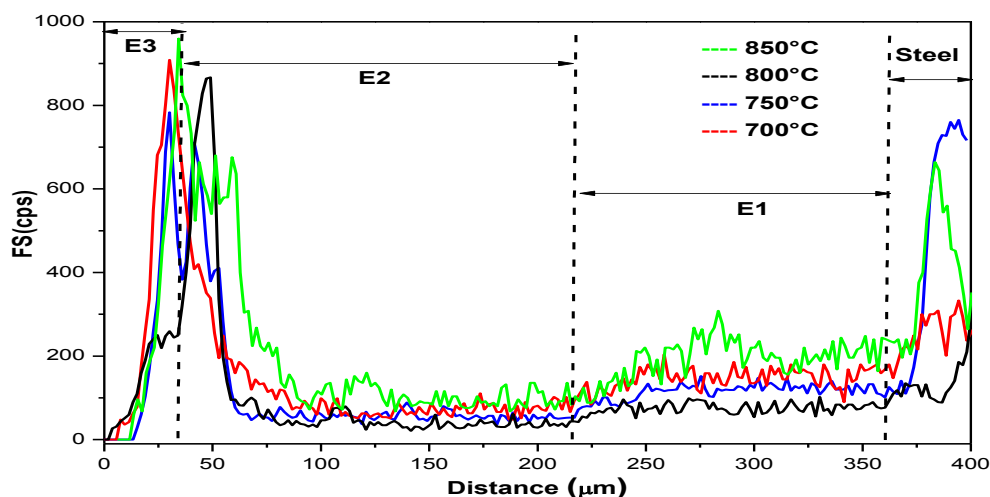


Figure 8: Diffusion of cobalt from the steel into the enamel measured by Line-Scan.

3.5. Microhardness

The microhardness of enamel enhanced greatly by the thermal treatment, as shown in Fig. 9. When the time is kept constant, microhardness of the enamel coating is improved slightly in the temperature range from 700 to 720 °C; then increases rapidly until reaches its peak value at 760 °C. Afterward it gradually declines with the further rise of firing temperature. The maximum hardness of the enamel coating reaches 5.85 Gpa at 760 °C for 4 min.

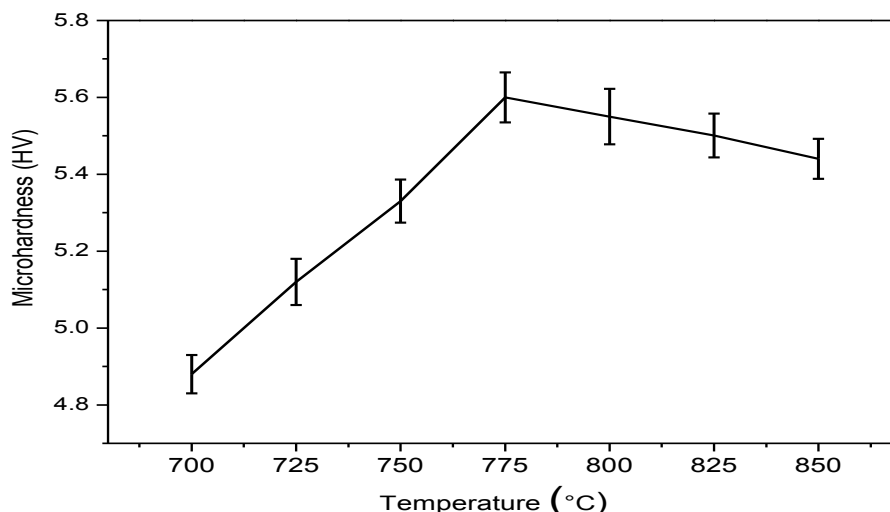


Figure 9: Effect of temperature on hardness of the enamel.

At each of the temperatures, the microhardness of the coating is different, which lies in the phase transformation which occurred in the coating during the treatment. As seen in Fig.9, the hardness of the enamel increased from 4.86 Hv to 6.6 Hv after firing between 700°C and 775°C, while it was slightly reduced when the firing temperature exceeds 775°C. The increase in the hardness was due to microstructural evolution. In according with X-ray diffraction analysis, the microstructure observation of the enamel steel reveals the existence of the

Al₂CoO₄ and SiO₂ crystals. Below 760°C, the nucleation rates of these phase is accelerated with the increase in temperature [25], resulting in a larger volume fraction of the SiO₂ and Al₂CoO₄ phases with numerous small crystals, thereby enhancing hardness of the enamel. Further increases in firing temperature for enamel caused a gradual decrease in hardness due to the disappear of SiO₂ phase and phase transformation [26]. When the crystals are small and homogenous in distribution, the hardness is the lowest owing to its little crystals. The agglomeration of particles during the enamel ageing resulting in the homogeneous coating layer seems to be the key factor controlling the mechanical properties.

Conclusion

The study reported in the present paper aims to increase the understanding of the characteristics and properties of the enamel–steel interface. Due to the fact that the enamel–steel interface is one of the most strategic and at the same time critical aspects that influence the quality and the behavior of the enamel coating, its understanding is crucial. The present study provided confirmation of the complex diffusion processes of material constituents that take place during enamel–steel system maturing at high temperature; it was discovered that such a diffusion process enabled the formation of some phase separations that can act as a nuclear agent for the crystallization of cristobalite rich phases. These cristobalite rich phases influence the adherence of the enamel as well as the hardness of the interface. By means of the nanoindentation techniques, the interface hardness was analyzed and a trend of increasing hardness from the steel side to the enamel one was observed.

References

1. Yang X., Jha A., Brydson R., Cochrane R.C., *Thin Solid Films* 443 (2003) 33.
2. Lawrence J., Li L., *Surf. Coat. Technol.* 140 (2001) 238.
3. Lawrence J., Li L., *Appl. Surf. Sci.* 138/139 (1999) 388.
4. Yatsenko E.A., Zubekhin A.P., Klimenko E.B., *Glass Ceram.* 61 (2004) 90.
5. Tsaur S.S., Yang, F.S., Shueh Y., You R., Shen P., *Mater. Sci. Eng. A* 165 (1993) 175.
6. Protasova L.G., Kosnyreva I.G., *Russ. J. Appl. Chem.* 77 (2004) 666.
7. Paparazzo E., Fierro G., Ingo G.M., Sturlse S., *J. Am. Ceram. Soc.* 71 (1988) C494.
8. Ubertazzi A., Wojciechowski N., *Vitreous enamel*, Hoepli Editor, Milan (2002).
9. Kautz K., *J. Am. Ceram. Soc.* 19 (1936) 93–108.
10. Ritchie D., Schaeffer H.A., White D., *J. Mater. Sci.* 18 (1983) 599.
11. Mackert Jr. J.R., Conner T.G., Ringle R.D., Parry E.E., Faihurst C.W., *J. Am. Ceram. Soc.* 75 (1992) 3087.
12. M. Peterson, Bernardin A.M., Kuhnen N.C., Riella H.G., *Mat. Sci. Eng.: A* 466 (2007) 183.
13. Brennan J.J., Pask J.A., *J. Am. Ceram. Soc.* 56 (1973) 58.
14. Errandonea D., Meng Y., Häusermann D., Uchida T., *J. Phys.: Condens. Matter* 15 (2003) 1277.
15. Abo-Naf S., El Batal F., Moenis A., *Mater. Chem. Phys.* 77 (2002) 852.
16. Bates J.B., *J. Chem. Phys.* 57 (1972) 4042.
17. Cherukuri S.C., Pye L.D., Chakraborty I.N., Condrate Sr. R.A., Ferraro J.R., Cornilsen B.C., Martin K., *Spectrosc. Lett.* (1985) 123.
18. Šimon I., McMahon H.O., *J. Chem. Phys.* 21(1953) 23.
19. Swainson I.P., Dove M.T., Palmer D.C., *Phys. Chem. Miner.* 30 (2003) 353.
20. Wen S.F., *Fourier Transform Infrared Spectrograph*, Chemical Industry Press, Beijing (2005).
21. Barcova K., Mashlan M., Zboril R., Filip J., Podjuklova J., Hrabovska K., Schaaf P., *Surf. Coat. Technol.* 201 (2006) 1836.
22. Pagliuca S., Faust W.D., *Porcelain (Vitreous) Enamels and Industrial Application and Propertied of Enamels*, (3rd ed.) International Enamellers Institute and Porcelain Enamel Institute, Tipografia Commerciale, Mantova, Italy (2011).
23. Shieu F.S., Lin K.C., Wong J.C., *Ceram. Int.* 25 (1999) 27.
24. Samiee L., Sarpoolaky H., Mirhabibi A., *Mat. Sci. Eng. A* 458 (2007) 88.
25. Goel AShaaban., E.RMelo., F.C.L., Ribeiro M.J., Ferreira J.M.F., *J. Non-Cryst. Solids* 353 (2007) 2383.
26. Kotan H., Darling K.A., Saber M., Koch C.C., Ronald O., *J. Alloys Compd.* 551 (2013) 621.

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