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Microstructure and adherence of porcelain enamel to low carbon steel

Fuh-Sheng Shieu*, Kuen-Chang Lin, Jen-Chyang Wong

Institute of Materials Engineering, National Chung-Hsing University, Taichung 402, Taiwan

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Abstract

Porcelain enamelled steel with various pretreatments was produced by a standard practice for evaluation of adherence using both conductivity measurement and periodic cracking method. From the test results, it was found that the adherence of porcelain enamel to steel treated with cobalt is higher than that treated with nickel and without transition metal. The difference in the adherence can be explained from an examination of the microstructure of enamel/steel interfaces by scanning electron microscopy. Good adherence is associated with those that have high density of anchor points at the enamel/steel interface. This suggests that the adherence of the porcelain enamel to steel is controlled by a mechanism of mechanical interlocking. In addition, a plot of the adherence index versus average shear stress shows a sigmoidal curve, within which the failure mode of the enamel changes from cohesive to adhesive at a critical load.

1. Introduction

Ceramic coatings have been an important research area in materials technology over the years and their applications cover from civilian industries to space technology. Coatings are applied to substrates for different purposes, e.g. improving corrosion resistance, wear resistance, barrier property, aesthetics, and so forth. Regardless of its end use, two important criteria must be satisfied for a coating to function properly during service; that is, good coating properties, e.g. physical, chemical and mechanical properties, and good adherence between coating and substrate. In general, coating properties are closely related to a material's bulk properties, which can be controlled by tailoring the chemical composition, microstructure, and residual stresses of the coating [1–4]. For example, the coefficient of linear thermal expansion of a porcelain enamel can be estimated using the rule of mixture from its major constituent oxides [1]. On the other hand, the adherence of coating to substrate is a somewhat complex issue and depends upon various factors such as pretreatments of a substrate before enamelling, which may involve surface modifications, interlayers, or interfacial reactions at the coating/substrate interface. Pickling and transition-metal (nickel or cobalt) dip are the common practices used by the enamel industry for improving the adherence of porcelain enamel to low carbon steels [5–7].

Various techniques have been proposed and utilised to evaluate the adherence of a ceramic coating to a substrate, e.g. indentation method [8], scratch test [9], bending test [10], and conductivity measurement [11]. Among them, the indentation method and the scratch test are popular in the field of thin-film technology, and are often used by production lines as a quality control tool. In contrast, the bending test and the conductivity measurement are widely accepted in thick-film technology, for instance, by enamel industry. Recently a periodic cracking method (see Section 3.2) for measuring the ultimate shear strength of a metal/ceramic interface was proposed by Agrawal and Raj [12]. This method has been applied to ceramic/metal systems such as SiO_2/Cu [12] and NiO/Pt [13] with planar specimen geometry for measurement of the interfacial shear strength, and it was shown experimentally that the method is best fit for systems that involved a brittle coating on a ductile substrate.

In this paper, two techniques, conductivity measurement and periodic cracking method, were used to evaluate the adherence of porcelain enamel to low carbon steel, by which the relationship between these two test methods was investigated. The microstructure of the

* Corresponding author.

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enamel/steel interfaces with different transition-metal treatments was studied by cross-sectional scanning electron microscopy (SEM).

2. Experimental Details

A SPP (special purpose for porcelain) grade low carbon steel, provided by the China Steel Co., Taiwan, was used as the substrate for this study. The nominal concentrations of C, Mn, P, S, Al, and Ti in the steel are 0.003, 0.16, 0.009, 0.005, 0.045, and 0.074%, respectively. Two different sizes of specimens were prepared: one has the dimensions of 100×100×0.8 mm used for conductivity measurement, and the other has an apparent size of 120×25×0.8 mm, by which a dumbbell-shaped specimen is made for tensile test on which the periodic cracking method is based. Before enamelling, the specimens were subjected to a series of pre-treatments, which may include (i) degreasing in a 5% Na_2SiO_5 solution at 70 °C for 40 min and then rinsing in running cold water for 4 min, (ii) pickling in a 14% H_2SO_4 solution at 70 °C for either 3, 6, or 9 min and then rinsing in running water for 4 min, (iii) cobalt or nickel dipping in a 14 g/l $CoSO_4$ or $NiSO_4$ solution at 70 °C for either 4 or 8 min, and (iv) neutralisation in a mixed solution of 1.2 g/litre Na_2CO_3 and 0.4 g/litre borax at 70 °C for 4 min, (v) drying in an oven at 100 °C for 30 min. The pH values of the $CoSO_4$ and $NiSO_4$ solutions were controlled between 10.5 and 11.0, and 3.0 and 3.5, respectively. A total of 15 groups of specimens, corresponding to different pickling time, types and soaking time of the transition-metal treatments, were prepared. The experimental conditions for each group of specimens are listed in Table 1.

Table 1
The experimental conditions and adherence test results of porcelain enamelled low carbon steels

Specimen group[a]	Periodic cracking method			PEI test
	λ_{avg} (μm)	δ (μm)	$\tau_{avg}(\sigma_f)$	Adherence index
SA3N0Z4G	278	73	1.65	3.0
SA3N4Z4G	366	71	1.22	5.3
SA3N8Z4G	340	85	1.57	4.1
SA3C4Z4G	242	85	2.20	89.3
SA3C8Z4G	234	73	1.96	90.5
SA6N0Z4G	340	91	1.68	3.6
SA6N4Z4G	405	72	1.12	5.9
SA6N8Z4G	448	91	1.28	4.7
SA6C4Z4G	261	98	2.36	74.0
SA6C8Z4G	313	99	1.99	91.1
SA9N0Z4G	370	95	1.61	5.3
SA9N4Z4G	435	90	1.30	4.7
SA9N8Z4G	517	70	0.85	5.3
SA9C4Z4G	417	115	1.73	21.3
SA9C8Z4G	390	100	1.61	60.3

[a] Characters S, A, C, N, Z, and G denote SPP steel, pickling in a 14% H_2SO_4 solution, cobalt bathing, nickel bathing, firing at 820°C, and ground coat, respectively. The number following characters A, C, N, and Z is the duration of the pretreatment in min.

Commercial frits 5205, 5206, and 5263 from Ferro Co., Japan, were ball milled separately down to 200 mesh and mixed, with equal part of each frit, with additives kaolinite, quartz, borax, $NaNO_2$ and water, to form a batch of enamel slip. The specific gravity of the enamelling slip is controlled between 1.6 and 1.67 by adjusting the water content, and the slip was aged for 36 to 48 h before enamelling to improve its fluidity. The enamel slip was then applied to the pretreated sheet steels by a hand-spraying system. The weight gain for each specimen after enamelling is about 33 mg mm^{-2}, resulting in a coating of thickness ~100 μm. The specimens were then dried in an oven at 150 °C for 30 min. Firing of the porcelain enamel was carried out in a box furnace at 820 °C for 4 or 6 min and then cooled in air.

The adherence of the porcelain enamel to the sheet steel was evaluated first using a conventional conductivity measurement which gives a number called adherence index. For those specimens with dumbbell shape, tensile test for evaluation of adherence was carried out in an Instron machine, from which the periodic cracks developed in the enamel upon tensile loading were observed. From the measured crack spacings, the average shear stress at the enamel/steel interfaces was estimated and it was compared with the conductivity measurement for specimens prepared in the same conditions. The surface topography of the enamelled specimens after aforementioned mechanical tests was examined by an Olympus PME3 microscope. To understand the microstructure of the enamelled steel produced with different transition-metal treatments, cross section specimens were prepared by a standard metallography procedure. Examination of the interfacial microstructure was carried out by a JEOL 5400 scanning electron microscope equipped with a Link energy dispersive spectrometer. The microscope was operated at an accelerating voltage of 15 kV and the electron micrographs were recorded using the backscattered electrons. The chemistry of the reaction products at the enamel/steel interfaces was analysed by an energy dispersive spectrometer which has energy resolution of 138 eV for Mn K_α.

3. Results and discussion

To provide a basic knowledge of the testing methods used to evaluate the adherence of porcelain enamels to low carbon steels, a brief description of the principle of the techniques along with the test results is given below.

3.1. Conductivity measurement—adherence index

This testing method was initiated in 1951 by the Porcelain Enamel Institute (PEI) of America and later in 1978 adopted by the American Society for Testing and Materials (ASTM) as a standard method for evaluation of the adherence of porcelain enamels and ceramic coatings to sheet metal [11]. Since then, it has been widely accepted by the enamel industry as a quality control tool for evaluation of the adherence of porcelain enamels to low carbon steel. To prepare for the conductivity measurement, a circular depression is first made on an originally flat enamelled sheet steel by a deforming press. In addition to cohesive failure where fracture of the enamel occurred owing to deformation, adhesive failure resulted from the delamination of an enamel from the steel substrate, can readily occur in systems where the bonding strength between enamel and steel is weak; thus the steel is exposed to the air. After cleaning the loosely bound enamel fragments from the steel substrate, conductivity measurement of the deformed specimens is made by an adherence meter

The adherence meter is an electronic instrument equipped with 169 needle-like probes assembled in a hexagonal pattern. Each probe is connected to an electric circuit, which will be completed through the grounded base metal of the specimen where the enamel (an insulator) is broken down completely and the base metal is in direct contact with the probe. Conductivity measurement is done by pressing the probe head against the depressed region of the specimen and counting the number of probes, X, which form complete circuits. The extent of adhesion between enamel and steel is expressed by an adherence index:

$$A = [(169 - X)/169] \times 100 \quad (1)$$

It can be easily understood that the higher the adherence index is, the better the adhesion of the enamel to the steel is.

The measured adherence indices for each group of the specimens are listed in the last column of Table 1. It can be seen that the distribution of the adherence index tends to be bimodal: Ni-dipped and untreated samples have low values, $A < 6$, whereas samples treated with cobalt have much higher numbers, $A > 60$, except for the group SA9C4Z4G which has $A = 21$. The use of transition-metal treatments in promoting adhesion between porcelain enamel and steel has been reported, e.g. by Richmond et al. [6,7], and it has become a standard practice in enamel industry, in particular for one-coating enamel on steel [14].

The surface of the depressed area in a cobalt-dipped specimen, as shown in Fig. 1(a), is covered with a layer of remnant enamel, which implies that the bonding strength of the enamel/steel interface is stronger than the fracture strength of the porcelain enamel; i.e. failure of the enamelled steel upon deformation is predominated by a cohesive mechanism. On the contrary, the depressed area of those treated with nickel and untreated samples looks lustrous as shown in Fig. 1(b). Since the bonding strength of the enamel/steel interface is weak, delamination of the enamel from the steel substrate can readily occur upon deformation, resulted in exposure of the base metal to air. In general, it is the cohesive failure that is favored for porcelain enamelled steels.

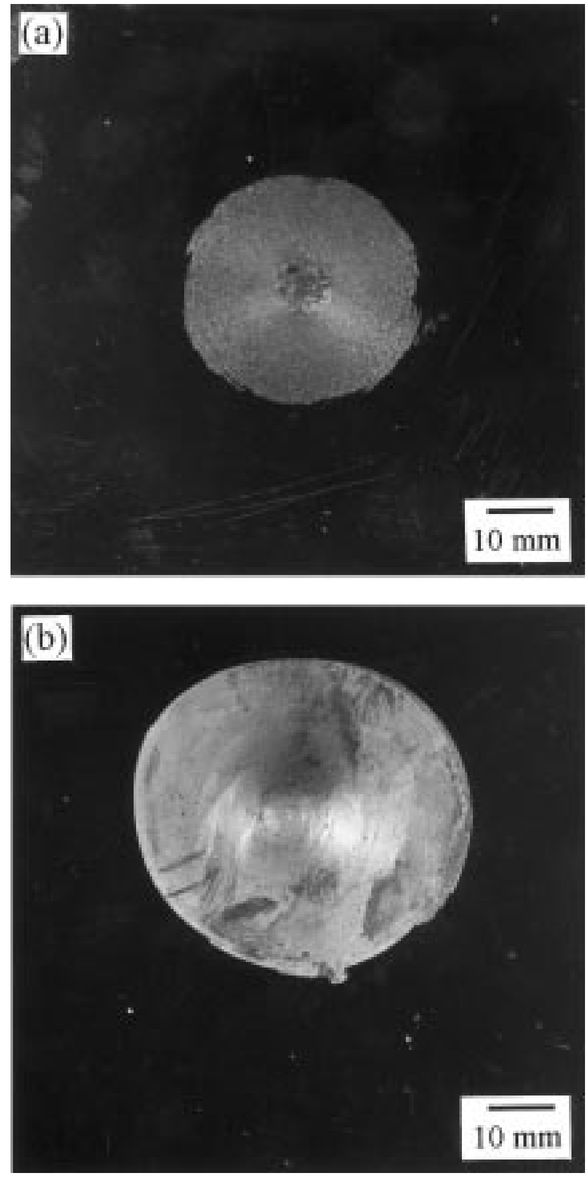

Fig. 1. Surface morphology of enamelled steels upon impact deformation for conductivity measurement, demonstrating the different appearance for specimens treated (a) with cobalt, (b) without transition metal.

3.2. Periodic cracking method

The periodic cracking method proposed by Agrawal and Raj has been applied to investigate the mechanical properties of ceramic/metal interfaces [12,13] and recently been extended to a polymer system [15] which involves a glassy polystyrene coating on a polycarbonate substrate. A detailed description of the method can be found in the original work of Agrawal and Raj [12]. Only a short summary will be outlined below.

For the specimen geometry of a brittle thin film deposited on a ductile substrate as shown in Fig. 2, when a load is applied to the substrate, shear stresses are developed in the vicinity of the interface, resulting from the difference in axial displacement when the thin film and the substrate were deformed separately. A normal tensile stress in the thin film is coupled to the shear stress at or near the interface through an integral equation

$$\sigma(\chi) = \frac{1}{\delta}\int_0^x \tau(x)\mathrm{d}x \tag{2}$$

where $\sigma(x)$ is the average tensile stress in the thin film, δ is the thickness of the thin film, τ is the shear stress at

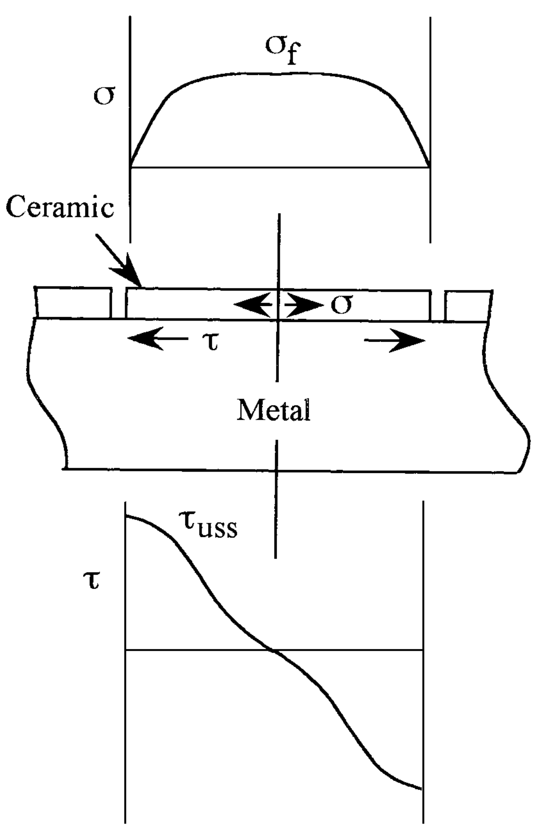

Fig. 2. A schematic diagram showing the stress distribution in a bi-layer specimen under applied tensile loading.

the interface and x is the coordinate along the interface with origin at the crack. From this force equilibrium equation, the ultimate shear stress, τ_{uss}, at the interface is obtained as

$$\tau_{uss} = \frac{\pi\delta\sigma_f}{\lambda_{max}} \tag{3}$$

where σ_f is the fracture strength of the thin film and λ_{max} is the maximum crack spacing in the thin film. Theoretically the crack spacings will range from λ_{min} (minimum crack spacing) to λ_{max} in which $\lambda_{max} = 2\lambda_{min}$ [12]. To simplify the analysis, an average crack spacing λ_{avg} is used in this study; thus the ultimate shear stress τ_{uss} on the left side of Eq. (3) would be the average shear stress, τ_{avg}, at the enamel/metal interface. For integration, a sinusoidal shear stress distribution with maximum located near the crack was assumed, resulted in the integration constant of π.

The average crack spacing, λ_{avg}, for each group of the specimens at 5% elongation and the corresponding averaged enamel thickness measured by cross-section scanning electron microscopy are also listed in Table 1, as well as the calculated average shear stress, τ_{avg}, using Eq. (3). The average shear stress in the table is expressed in terms of the fracture strength of the enamel, σ_f, which was measured to be in the range of 1.5 to 2.4×10^8 Pa from the crack density versus elongation curve of the tensile test specimens using the periodic cracking method [12,13].

From Table 1, it can be seen that the average shear stress at the enamel/steel interfaces spans from 0.85 to $2.36\,\sigma_f$. Similar to the results of conductivity measurement, the average shear stress of the cobalt-dipped specimens is higher than that treated with nickel and without transition-metal treatment, except for the group SA9C8Z4G which has $\tau_{avg} = 1.61\,\sigma_f$, lower than some of the non-transition-metal treated specimens. A typical optical micrograph of the periodic cracks developed in a cobalt-dipped specimen at 5% elongation is shown in Fig. 3. It is also noted from the test results that for those specimens having $\tau_{avg} < 1.5\,\sigma_f$ an adhesive failure was observed in the enamelled steel, whereas for those specimens having $\tau_{avg} > 1.8\,\sigma_f$ damage of the enamel upon tensile loading was mainly by cohesive failure. A mixed mode of failure was observed for those having τ_{avg} in between, e.g. group SA9C8Z4G.

3.3. Microstructure of enamel/steel interfaces

Mechanical test either by conductivity measurement or periodic cracking method has shown that the adherence of enamel to steel depends considerably on the types of transition-metal treatment before enamelling. It is therefore of interest to understand the relation between microstructure and adherence of the enamelled steel, and the influence of transition-metal treatments on the microstructure of enamel/steel interfaces. A typical SEM micrograph of the enamel/steel interface of a specimen in group SA3N0Z4G, using backscattered electrons for imaging, is shown in Fig. 4(a). As a result of the pickling procedure, the enamel/steel interface displays some degree of roughness. Increasing the pickling time from 3 to 9 min in the 14% H_2SO_4 solution did not seem to make any significant change on the roughness of the interface. Fig. 4(b) gives the SEM micrograph of a specimen from group SA3N4Z4G which was treated with nickel before enamelling. Unlike Fig. 4(a), an interlayer $\sim$ 2 2 μm thick, resulted from interfacial reactions, is present between enamel and steel. The interlayer shows contrast similar to that of the steel substrate, which implies that the average atomic number of the interlayer is similar to that of the steel substrate, and is almost separated from the steel substrate. Analyzed by an energy dispersive spectrometer (EDS) as shown in Fig. 5(a), it was found that the interlayer is mainly composed of Fe and Ni. Examination of the interfacial microstructure of the other nickel-dipped specimens revealed that the interlayer would break into segments and appear further away from the interface as the time of picking and nickle dip increased. For example, a specimen from group SA9N8Z4G displayed an interfacial microstructure, in which many irregular Fe–Ni islands, instead of an interlayer, were dispersed within 10 μm from the steel substrate.

Fig. 4(c) shows the SEM micrograph of a cobalt-dipped specimen from group SA3C4Z4G. The morphology of the enamel/steel interface is considerably different from that of either untreated (Fig. 4(a)) or nickel-dipped specimen (Fig. 4(b)). Interfacial reactions among cobalt, enamel, and steel during firing produced many small islands within $\sim$ 2 μm from the steel substrate. From the SEM micrograph of Fig. 4(c), it can be seen that the islands are interconnected and form the so-called anchor points; thus the roughness of the interface is increased. Improvement of the adherence of the enamel to steel by mechanical interlocking was also reported by other investigators. [6,16] The chemical composition of the islands analysed by EDS is shown in Fig. 5(b), in which the Co K_{α} overlaps with Fe K_{β}. Similar to the Fe–Ni interlayer in Fig. 4(b), interfacial reactions among enamel, cobalt, and steel give rise to the formation of the Fe–Co alloy. However, it can be seen from the EDS spectra that the Co content in the Fe–Co islands is lower than that in the Fe–Ni interlayer.

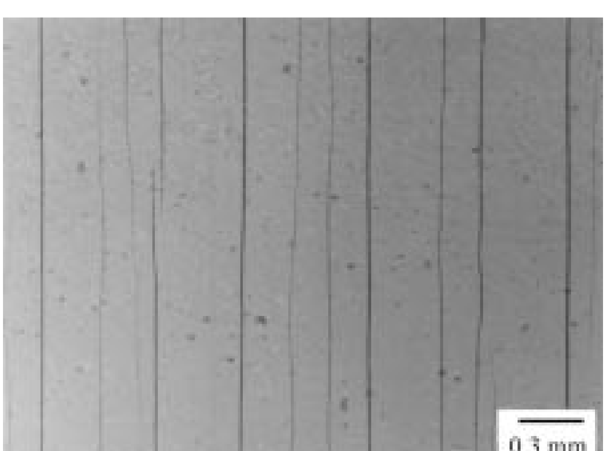

Fig. 3. An optical micrograph of the periodic cracks developed in the enamel of a cobalt-dipped specimen upon applied tensile loading.

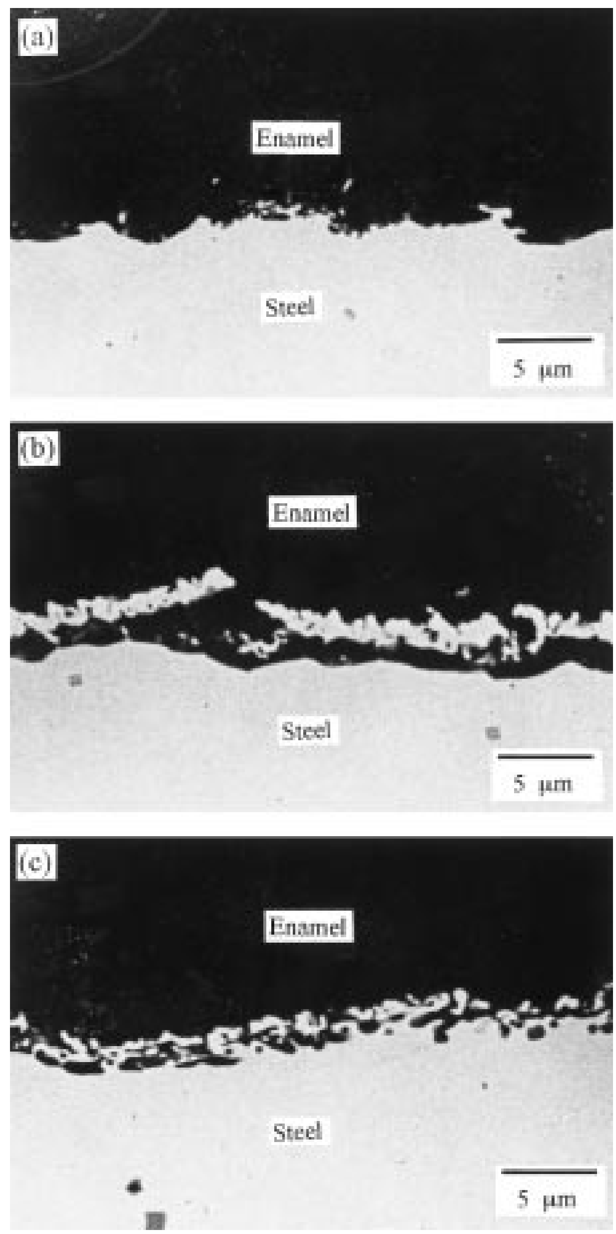

Fig. 4. Cross-sectional SEM micrographs of enamel/steel interfaces, in which the steel was treated (a) without transition metal, (b) with nickel, resulted in a Fe–Ni interlayer $\sim$ 2 mm thick appear near the interface, and (c) with cobalt, resulted in the presence of Fe–Co islands at the interface and formed the so-called anchor points.

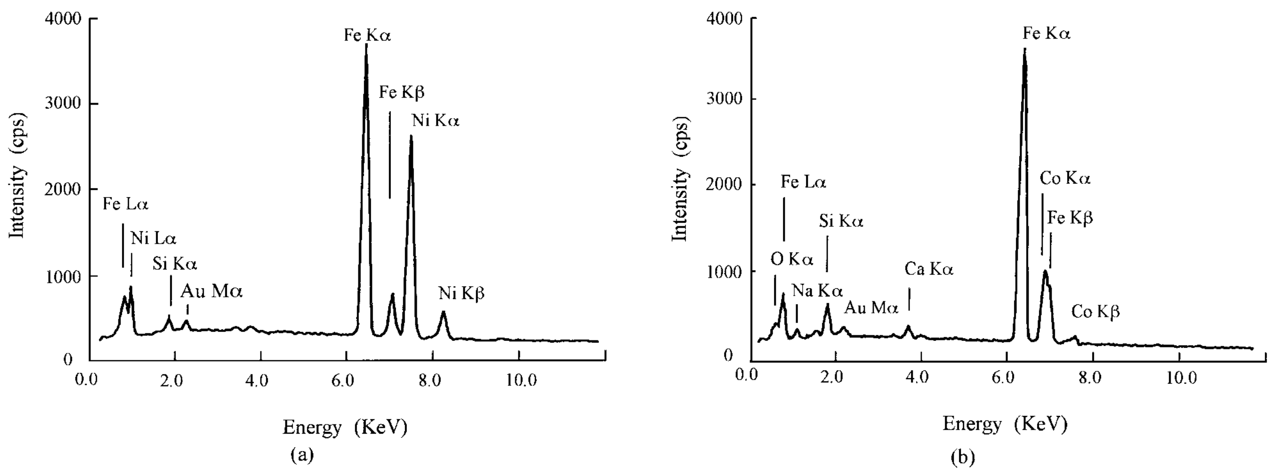

Fig. 5. Typical EDS spectra of (a) the Fe–Ni interlayer in a nickel-dipped specimen, and (b) the Fe–Co islands in a cobalt-dipped steel.

From examination of the interfacial microstructure by SEM, it can be concluded that good adhesion is usually associated with those specimens that have an interface with high density of anchor points, whereas poor adhesion occurs in those specimens that show roughness of large periodicity or that has interlayers which are detached from the substrate as a result of over-reaction. Several studies [5–7] have shown that the adherence of porcelain enamels to steels is closely related to the roughness of the enamel/steel interface, which can be caused by either mechanical, chemical or electrochemical processes, e.g. sandblasting, pickling, and interfacial reactions or galvanic corrosion due to the presence of transition metals at the interface. It is, however, important to note that although the experimental result of this study demonstrates that the adherence of porcelain enamel to steel is controlled by a mechanical interlocking mechanism, other evidences [6,7] in the literature showed that good adherence has been obtained without surface roughening.

3.4. A comparison between conductivity measurement and periodic cracking method

From the results of adherence test in Table 1, it is found that application of pretreatments has pronounced effects on the adherence of porcelain enamel to the sheet steel under the specified processing conditions. Specimens treated with cobalt showed very good adhesion, i.e. high adherence indices. This is also reflected from the measured average shear stresses, which are higher than 1.61 σ_f. For those specimens used for conductivity measurement, an adhered layer of the enamel remained on the depressed region of the steel, as shown in Fig. 1(a). On the contrary, the specimens either treated with nickel or without transition metal exhibited very low adhesion. This is illustrated by the fact that the adherence indices of these specimens are considerably low, ~ 5, and the base metal in the depressed region of the enamelled specimens is completely exposed. Compared with those treated with cobalt, the average shear stresses of these specimens are also relatively low, and span a wide range from 0.85 to 1.68 σ_f.

A diagram showing adherence index A vs average shear stress τ_{avg} is given in Fig. 6. It seems that the adherence indices follow a bimodal distribution, whereas the values of the average shear stress vary gradually. Qualitatively, it might be claimed that there exist a proportional relation between these two parameters; that is, specimen having good adherence index also exhibits high average shear stress. In fact, from the distribution of the data points, their relation is more likely to be simulated by a sigmoidal curve as depicted in Fig. 6 except the data points at the upper right region of the diagram which do not fit well into a horizontal line. In other words, it suggests that there exists a critical average shear stress, $\tau_{cavg} = 1.61\, \sigma_f$, across which the adherence index increases rapidly. From examination of the specimen surface after adherence test, it can be found that this critical average shear stress reflects a change of failure mode in the porcelain enamel; i.e. at $\tau_{avg} < \tau_{cavg}$ adhesive failure prevails, whereas at $\tau_{avg} > \tau_{cavg}$ cohesive failure dominates.

It is useful to examine the deformation mechanisms involved when the specimens were prepared for conductivity measurement and periodic cracking method. Before the conductivity measurement was carried out, an enamelled specimen was first deformed by a steel ball of 25 mm in diameter under a load of 8884 N to form a dimple. From the view point of the enamel/steel interface, the applied load is mainly normal to the interface. This is different from that of the periodic cracking method, in which the interface experiences a shear stress upon applied tensile loading. Since the state of stress experienced by the interface is different, the values of adherence index and average shear stress would reflect the resistance of the interface to normal and shear stress, respectively. Fig. 7 shows two modal enamel/steel interfaces having the same periodicity but with different wave shape. Mechanical interlocking is said to be present in Fig. 7(b), but not in Fig. 7(a). Since the two interfaces have similar roughness and periodicity, it is expected that they would show similar average shear stress. This won't be the case for the adherence index. Assuming that the intrinsic bonding strength between enamel and steel is the same for the two types of interfaces, interface having anchoring points such as Fig. 7(b) could withstand much higher normal stress perpendicular to the interface than that of Fig. 7(a). As a result, under similar testing conditions, specimens having microstructure like Fig. 7(a) would show adhesive failure, i.e. low adherence index, whereas specimens having microstructure like Fig. 7(b) would show cohesive failure, i.e. high adherence index.

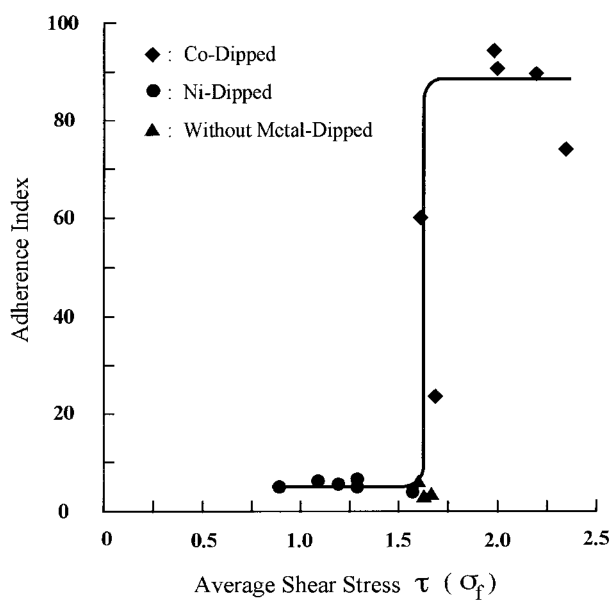

Fig. 6. Correlation between adherence index and average shear stress of a porcelain enamelled steel, measured by conductivity measurement and periodic cracking method, respectively.

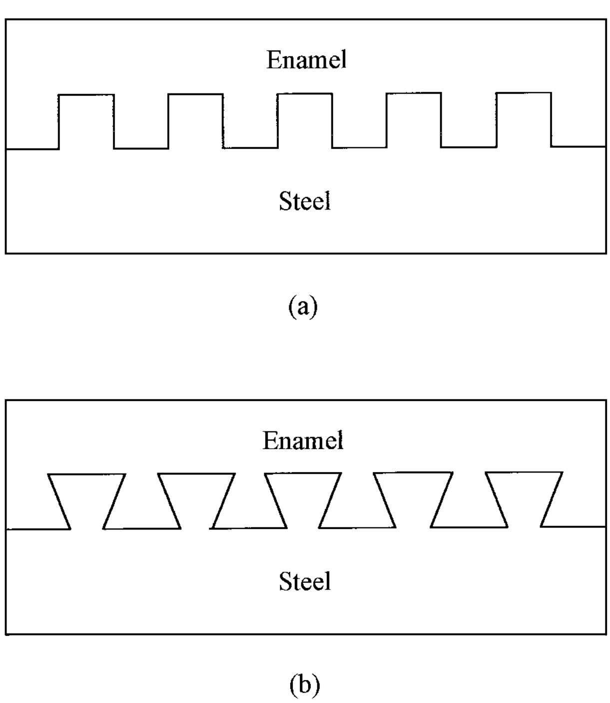

Fig. 7. Schematic diagrams showing two modal enamel/steel interfaces having (a) roughness of square wave, and (b) wedge-shaped wave illustrating anchor points.

4. Conclusions

Two techniques, conductivity measurement and periodic cracking method, were used to evaluate the adherence of porcelain enamel to low carbon steel with different pretreatments. It was found from the test results that the adherence of porcelain enamel to steel treated with cobalt is higher than those treated with nickel and without transition metal. The difference in the adherence can be explained from an examination of the microstructure of enamel/steel interfaces by scanning electron microscopy. Good adherence is associated with those that have high density of anchor points at the enamel/steel interface. This suggests that the adherence of the porcelain enamel to steel is controlled by a mechanism of mechanical interlocking.

Examination of the fracture surface of the enamelled steel upon deformations revealed that the failure mode of the enamel for the cobalt-dipped specimens was mainly cohesive, whereas it was adhesive for the other specimens. In addition, a plot of the adherence index versus average shear stress shows a sigmoidal curve, within which the failure mode of the enamel changes from cohesive to adhesive at a critical load. This critical load occurs when the measured average shear stress, τ_{avg}, is equal to 1.61 σ_f.

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