Adhesion of Enamel Layer after Repeated Firings in Ti-Stabilized IF Steel Sheet for Porcelain Enamel Use and Its Mechanism

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Adhesion of enamel layer in Ti-stabilized Interstitial-Free steel (Ti-IF) for porcelain enamel was studied through pickling loss weight, smuts on a pretreated Ti-IF steel, chemical compositions of steel and the repeated number of firing to form enamel, comparing with high oxygen steel for porcelain enamel.

When pickling loss weight in Ti-IF steel is below 30 g/m², the adhesion of enamel layer can be over 80 % even after firing is repeated four times. High oxygen steel, in contrast, has over 80 % adhesion of enamel layer, regardless of the repetition of firing, and its adhesion is not related to pickling loss weight.

TEM observation reveals that the smut on pretreated Ti-IF steel is mainly round-shaped TiS (100–300 nm) and the one on pretreated high oxygen steel is mainly Cr₇MnO₄ (100–300 nm). During the reaction between enamel and pretreated steel for firing process, TiS is presumed to worsen adhesion, while Cr₇MnO₄ is not related to adhesion. Therefore, reducing TiS (lowering pickling loss weight) is an effective measure to keep satisfactory adhesion in Ti-IF steel at repeated firings.

Under conventional pretreatment conditions (ex. pickling for about 5 min with 12–15 % H₂SO₄ at 70–80°C and Ni-deposition for about 5 min with 13–18 g/L NiSO₄·7 H₂O at 70–80°C), Cu should be higher than about 0.04 % and P should be lower than about 0.013 % to be below 30 g/m² as pickling loss weight in order to keep over 80 % adhesion in Ti-IF steel.

KEY WORDS: porcelain enamel; pickling weight loss; PEI adhesion; smut; Ti-IF steel; copper; phosphorus.

1. Introduction

Ti-stabilized Interstitial-Free steel (Ti-IF) for porcelain enamel has good formability, and it is needed for high formable wares, especially bathtubs and washbowls. Recently, as some of the high formable enamels are shifted to more deep-drawable designs and larger sizes, enamel-related defects sometimes occur in the enamel process when evaluated in a unit of an enamelware, although the frequency is almost the same if evaluated in the total area of enamel products. Therefore, present-day enamels are sometimes fired once or twice more to repair the defects, although they are said to be produced by 2-coat-2-fired (2C2F) way, as shown in Fig. 1.

In some cases, the adhesion of enamel layer on Ti-IF steel is degraded as the firing process is repeated. Especially, the adhesion at the corner and the flange in a large enamelware is lowered, and as shown in Fig. 2, sometimes its enamel layer comes off, showing a “silver sheen” when fired more than three times.

Figures 3(a) and 3(b) show cross-sectional optical micrographs at an enamel-sticking part near peeled-off area and at a high adhesive enamel layer, respectively. At the boundary between enamel and steel, the area with low adhesion has a film-like structure but the one with high adhesion has a rugged and rough structure in which steel and enamel are mutually up and down. As shown in Fig. 4, something blackish sticks on a pretreated surface of such a low adhesive area as seen in Fig. 3(a), but these things have not been precisely characterized, because sticking stuffs on the surface are so thin that they are affected by steel substrate even if evaluated with XRD and SEM-EDX.

The phenomena to degrade adhesion at the repetition of firing occur only in deep-drawable and larger enamelwares, which have been recently produced. Therefore, reports have not mentioned these problems and their mechanisms. However, general theories to deteriorate adhesion in Ti-IF steel have been mentioned in some papers1–7): film-like or excessive smut of FeSO₄·7 H₂O,1,2) smut of TiFe₂O₄,3–5) solute Ti6) and increment of smut by increment of Ti addition.7) Smuts sticks thinly on pretreated Ti-IF steel and are entangled with Fe-related oxide and/or Ni-related residues. Therefore, smuts have not been precisely determined with SEM and XRD and so their theories include estimation. As
for TEM, it has not been used for analysis of smut, because its sample preparation is difficult.

Also, the phenomenon to degrade adhesion in Ti-IF steel has been known in the enamel industry, apart from the deterioration of enamel layer at the repetition of firing. In foreign countries, a countermeasure is sometimes taken by "pickling with dilute H$_2$SO$_4$ (5–8%)" on the prerequisite condition that only Ti-IF steel is used in process line. In Japan, however, enamelwares are often assembled with different kinds of enamel steel, or enamel process line is shared with other kinds of enamel steel rather than used only for Ti-IF steel. Therefore, pickling has been done with 12–15% H$_2$SO$_4$ for 3–5 min in enamelmakers in Japan. It should be noted that process-line speed is fixed in each enamelmaker, and pickling weight loss can not be adjusted by changing its speed.

In this paper, the adhesion in Ti-IF steel is discussed when it is pretreated with highly concentrated “17% H$_2$SO$_4$” for 4 min. “17% H$_2$SO$_4$” is a little higher than conventional in Japan and its density is such an extreme concentration that enamelmakers are reluctant to use in operation for Ti-IF steel. Under this extreme pickling condition, the deterioration of adhesion in Ti-IF steel at the repetition of firing is reported, comparing high oxygen steel which is known for high adhesion.

Additionally, a mechanism to improve the adhesion is discussed from the viewpoints of pickling loss weight, the observation of smuts on pretreated Ti-IF steel with TEM, and optimized chemical compositions.

2. Experimental Procedure

2.1. Effect of Time-controlled Pickling Weight Loss to Adhesion at Repeated-firing

Adhesion of Ti-IF steel at the repetition of firing was investigated in the viewpoint of pickling weight loss by changing time at 78°C with 17% H$_2$SO$_4$, comparing with high oxygen steel. Also smuts on pretreated Ti-IF and high oxygen steel were analyzed to know a factor to degrade adhesion.

As shown in Table 1, Ti-IF steel for porcelain enamel &
high oxygen steel\textsuperscript{8–12} were used for the analysis of adhesion at repeated firing conditions. These steel sheets were factory-products: 900 and 880°C in finishing temperature (FT), 640 and 620°C in coiling temperature (CT) at hot-rolling process, about 70% of cold reduction ratio, annealed at 850°C in Continuous Annealing Line (CAL) and 0.5 and 1.0% skinpass-rolled, respectively. It should be noted that these two steels are alloy-designed to suppress the occurrence of fishscales by many large-sized precipitates and inclusions: Ti-IF includes about 300 ppm of S and about 100 ppm of N and high oxygen steel includes about 500 ppm of oxygen.

100×100 mm-sized coupons were cut from these samples, and the experimental details are shown in Fig. 5. Only key points are emphasized as follows: (1) Pickling was done at 78°C with 17% H\textsubscript{2}SO\textsubscript{4} by controlling time: (1, 2, 4 and 10 min), (2) Ni flush was done at 82°C for 4 min in pH 2.8 with 15 g/L NiSO\textsubscript{4}·7H\textsubscript{2}O, (3) Slip was “H” (ground coat of 2-coat-2-fire, Japan Ferro Co./renamed as “TOMATEC” since Oct. 1, 2003) for Ti-IF & high oxygen steel and “1553B” (direct-on coat, Japan Ferro Co./renamed as “TOMATEC” since Oct. 1, 2003) only for high oxygen steel. Each blending was shown in Table 2. These slips were sprayed on steels. Thickness after fired was controlled to 100 μm on both sides. (4) Firing was done at 850°C for 5 min in 30°C dewpoint for ground-coat “H” and at 830°C for 5 min in 30°C dewpoint for direct-on “1553B”. When a sample was fired more than two times, it was baked again after it had cooled down to room temperature. Then samples were evaluated with PEI adhesion to pickling loss weight at the number of firing. Note that “30°C dewpoint” is an excessive condition to lower adhesion.

Also, smuts on 4-min-pickled and Ni-flushed Ti-IF and high oxygen steel are directly observed and analyzed with Transmission Electron Microscopy (TEM). Its sample preparation was a two-step extraction-replication\textsuperscript{13} with carbon evaporated film on a Cu-grid. Smuts on the as-pre-treated samples were taken off with a cellophane sheet and then smuts were directly observed without any interference of steel substrates. The important point for its sample preparation is that time of pickling is optimally conditioned for a proper quantity of residues and these particles are weakly bonded with Ni-compounds by Ni-flush process.

### 2.2. Pickling Loss Weight by Changing Cu and P Contents and Improvement of Its Adhesion

The improvement of adhesion was investigated by reducing pickling loss weight through the optimization of Cu and P contents in the Ti-IF steel for porcelain enamel. As shown in Table 3, samples with various sets of Cu and P in chemical compositions were prepared in a laboratory-scale vacuum-melting furnace. They were hot-rolled to about 3 mm thick at 890°C in FT, put at 640°C for 1 h in a furnace and

| Degreasing | 50g/L sodium silicate at over 90 deg C for 10 min |
| Rinse | with Hot water and then overflowing water (RT) |
| Pickling | by time controlling: 1, 2, 4 and 10 min at 76 deg C with 17% H\textsubscript{2}SO\textsubscript{4} |
| Rinse | with overflowing water (RT) |
| Ni flush | for 4 min at 82 deg C in pH2.8 with 15g/L NiSO\textsubscript{4}·7H\textsubscript{2}O |
| Neutralization | with Na\textsubscript{2}CO\textsubscript{3} and NaNO\textsubscript{2} in deionized water |
| Rinse | |
| Coating | “H” for ground-coat to Ti-IF & high oxygen steel |
| “1553B” for direct-on to high oxygen steel |
| Drying | |
| #1 Firing | at 30 deg C dewpoint (for Ti-IF & high oxygen) |
| #2 Firing | “1553B” for 5 min in 830 deg C at 30 deg C dewpoint (for high oxygen/direct-on) |
| #3 Firing | |
| #4 Firing | |
| (PEI adhesion) | |

**Fig. 5.** Procedure of adhesion test by using test piece (100×100 mm).

| C | Si | Mn | P | S | Sol Al | N | Cu | Ti |
|---|---|---|---|---|---|---|---|---|
| 0.001P & 0.020-0.050Cu | 0.0011 | 0.01 | 0.12 | 0.001 | 0.028 | 0.032 | 0.0097 | 0.020 | 0.110 |
| 0.0019 | 0.01 | 0.12 | 0.001 | 0.028 | 0.029 | 0.0109 | 0.030 | 0.101 |
| 0.0012 | 0.01 | 0.13 | 0.002 | 0.024 | 0.035 | 0.0072 | 0.039 | 0.103 |
| 0.0008 | 0.01 | 0.13 | 0.008 | 0.026 | 0.037 | 0.0076 | 0.021 | 0.105 |
| 0.008P & 0.020-0.050Cu | 0.0017 | 0.01 | 0.13 | 0.008 | 0.027 | 0.036 | 0.0081 | 0.030 | 0.102 |
| 0.0015 | 0.01 | 0.13 | 0.008 | 0.030 | 0.042 | 0.0089 | 0.039 | 0.106 |
| 0.0015 | 0.01 | 0.13 | 0.008 | 0.025 | 0.040 | 0.0081 | 0.045 | 0.102 |
| 0.0012 | 0.01 | 0.13 | 0.012 | 0.022 | 0.037 | 0.0088 | 0.020 | 0.103 |
| 0.0018 | 0.01 | 0.13 | 0.011 | 0.027 | 0.037 | 0.0103 | 0.030 | 0.104 |
| 0.0018 | 0.01 | 0.14 | 0.011 | 0.021 | 0.042 | 0.0089 | 0.040 | 0.106 |
| 0.0016 | 0.01 | 0.12 | 0.011 | 0.029 | 0.040 | 0.0081 | 0.049 | 0.103 |
| 0.012P & 0.020-0.050Cu | 0.0017 | 0.01 | 0.13 | 0.016 | 0.028 | 0.041 | 0.0083 | 0.021 | 0.102 |
| 0.0025 | 0.01 | 0.13 | 0.015 | 0.028 | 0.039 | 0.0081 | 0.030 | 0.099 |
| 0.0015 | 0.01 | 0.13 | 0.016 | 0.030 | 0.035 | 0.0078 | 0.039 | 0.100 |
| 0.0016 | 0.01 | 0.13 | 0.016 | 0.030 | 0.034 | 0.0087 | 0.049 | 0.100 |

**Table 3.** Chemical compositions of Ti-IF steel prepared in laboratory.
then cooled down in furnace (simulated CT: 640°C). They are mechanically polished to 2.8 mm thick and then cold-rolled to 0.8 mm thick. Annealing was done for recrystallization in a furnace in Ar gas environment, and skinpass-rolling was done at 0.5%. Five coupons (100×100 mm) from each sample were pickled for 4 min at 78°C with 17% H₂SO₄ and evaluated for an average pickling loss weight. The reason to choose such an over-pickled condition is to evaluate the pickling loss weight that can be expected in the most extreme cases in a real manufacturing process.

Four samples with different pickling loss weight were chosen among these Cu and P-optimized Ti-IF steel in order to investigate adhesion at the repetition of firings: (a) 0.045%Cu–0.011%P (35 g/m²), (b) 0.050%Cu–0.016%P (30 g/m²), (c) 0.050%Cu–0.011%P (25 g/m²), (d) 0.030%Cu–0.001%P (18 g/m²). Additionally, as-CAL sample (Table 1) was also used for reference whose composition and pickling weight loss are 0.033%Cu–0.011%P and 56 g/m², respectively.

Adhesion of these five sheets at the repeated firings was investigated in the procedure that is basically described in Fig. 5. The exception is that pickling was done only for 4 min and also only “H slip” was used.

Please note that pickling weight loss was controlled with chemical compositions (Cu and P) and the pickling condition was only for 4 min, although in Sec. 2.1, pickling weight loss is controlled with time (1, 2, 4 and 10 min).

3. Results

3.1. Effect of Time-controlled Pickling Weight Loss to Adhesion at Repeated-firing

Figure 6 shows PEI adhesion to pickling weight loss in Ti-IF steel and high oxygen steel by using 100×100 mm coupons when ① pickled for 1, 2, 4 and 10 min at 78°C with 17% H₂SO₄, ② Ni-flushed for 4 min at 82°C in pH 2.8 with 15 g/L NiSO₄·7H₂O and ③ repeated by firing ground-coat (G/C of 2-coat-2-fire) at 850°C for 5 min for Ti-IF and high oxygen steel and direct-on at 830°C for 5 min only for high oxygen steel.

As firing repeats, adhesion in Ti-IF steel, on the whole, decreases. Its adhesion becomes worse as Ti-IF steel for porcelain enamel is pickled longer. Especially at 10-min-pickled Ti-IF steel (pickling weight loss: 115 g/m²), adhesion is below an approved level at more than twice firing, judging from over 60–70% adhesion at worst generally accepted in the market. In contrast, high oxygen steel always keeps a high adhesion of around 90% in ground-coat “H”, and also in direct-on “1553B” if pretreated properly. The repetition of firing and pickling loss weight does not affect the adhesion of high oxygen steel.

Furthermore, smut was directly determined through the observation of replica samples by TEM equipped with EDX. Figure 7 shows smut on pretreated Ti-IF steel and high oxygen steel when pickled for 4 min at 78°C with 17% H₂SO₄ and Ni-flushed for 4 min at 82°C in pH 2.8 with 15 g/L NiSO₄·7H₂O.

It should be noted that TEM sample preparation is very difficult in shorter and longer pickling time than about 4 min in this pretreatment condition and also that Ni-flush is not omitted for it. The point is that residues on pretreated steel is properly scattered and they are weakly bonded with Ni-compounds to prepare replica samples. When pickled for 1 or 2 min, residues are so small in number that these data can not be related to enamel properties. Conversely, when pickled for 10 min, replica samples can be prepared in a rare case and supporting films are often broken away. Even if it can be prepared, residues are so complexly piled up each other that TEM images are almost black in all area and that residues can not be observed with TEM. Also, supporting carbon film would be broken easily without Ni-flush. Therefore, we determine the smuts only by using 4 min-pickled and 4 min-Ni-flushed samples, and we analyze them by omitting uniformly-entangled Ni-related materials as a common phenomenon in smut at all kinds of steel sheet for porcelain enamel.

In both steels, smuts are composed of precipitates of entangled Ni-related and Fe-related residues. The smut is TiS in Ti-IF steel and is Cr₅MnO₈ in high oxygen steel. As mentioned above, smut is larger in number as Ti-IF steel is pickled longer. Additionally, Fig. 6 shows that the adhesion of Ti-IF steel is deteriorated as Ti-IF is pickled longer. Therefore, the cause for the degraded adhesion in Ti-IF is presumed to be TiS on the pretreated surface, although TiS itself has never been mentioned in any reports. This evidence is also backed up with Ref. 14 which says that adhe-
sion in Ti-IF is improved when some of smuts are melted away with acid.

The above results can lead to two presumptions: (1) Pickling loss weight should be lower than 30 g/m² to keep high adhesion in Ti-IF steel even at the repetition of firing. If it is estimated on the safe side, pickling loss weight is advisable to be much lower, for example, below 20–25 g/m². (2) Also, the kind of smut and its quantity are important factors to adhesion for Ti-IF steel. Since the increment of pickling weight loss corresponds to the increase of smut, TiS should be reduced by decreasing pickling loss weight in order to keep good adhesion. The smut of high oxygen steel, in contrast, does not degrade its adhesion.

On the assumption that an enamel process line is shared with other kinds of enamel steel and pickled with highly concentrated “17 % H₂SO₄” for about 4 min, which is widely used in Japan, pickling properties should be lowered by optimizing chemical compositions in order to improve adhesion.

3.2. Pickling Loss Weight by Changing Cu and P Contents and Improvement of Its Adhesion

Figure 8 shows pickling loss weight to the content of Cu and P when pickled for 4 min at 78°C with 17 % H₂SO₄. Note that these samples were prepared in laboratory. Pickling loss weight is low when Cu content is high and/or P content is low.

In order to be below 30 g/m² of pickling loss weight, Cu should be higher than about 0.04 % and P should be lower than about 0.013 %. This result, together with Fig. 8, suggests that over 80 % adhesion can be achieved in Ti-IF steel for porcelain enamel even at repeated firings.

Five samples were picked up among the samples in Fig. 8 to investigate adhesion after repeated firings: (a) 0.045%Cu–0.011%P (35 g/m²), (b) 0.050%Cu–0.016%P (30 g/m²), (c) 0.050%Cu–0.011%P (25 g/m²), (d) 0.030%Cu–0.001%P (18 g/m²) and (e) As-CAL sample (Table 1) for reference, whose composition and pickling weight loss are 0.033%Cu–0.011%P and 56 g/m², respectively. Note that this pickling control by elements (Cu and P) is different from by pickling time in Fig. 6.

Figure 9 shows adhesion to the repeated number of firing in each pickling loss weight condition when pickled for 4 min at 78°C with 17 % H₂SO₄, Ni-flushed for 4 min at 82°C in pH 2.8 with 15 g/L NiSO₄·7H₂O, coated 100 μm on both sides with “H” slip (Table 2) and repeated the firing.
4. Discussion

Adhesion of enamel layer to steel has been explained with a mechanical and/or chemical aspect. In this paper, adhesion in Ti-IF steel for porcelain enamel at repeated firings is reported. As mentioned above, the origin to degrade adhesion must be “TiS” on pretreated Ti-IF steel. It is supported by the TEM micrograph of Fig. 7 and the adhesion to pickling loss weight at the repetition of firing of Figs. 6 and 9. Additionally, considering the results in Ref. 14 which says that adhesion in Ti-IF is improved when some of smuts are melted away with acid, we can lead a conclusion that the factor to deteriorate adhesion is “TiS”.

This mechanism is applied to the deterioration of adhesion in Ti-IF steel (not at repeated firings) which has been explained with some different concepts, and these theories are compared each other as follows;

Some researchers have said that Fe- and Ni-related oxide and sulfate are the causes of degraded adhesion. However, these deposits are common in all kinds of steel sheets for porcelain enamel, including high oxygen steel. Therefore, it is difficult to say that these materials are origins to degrade adhesion even if their existence is determined with low-angle XRD. Since the phenomenon to deteriorate adhesion at the repetition of firing is limited only in Ti-IF steel, the cause is presumed to a Ti-related substance.

Our estimation is based on TEM observation of smuts without any interference of steel substrate, by sample-prepared with two-step extraction-replication. In TEM analysis, we could not find TiFe2O4 which some people have concluded to be an origin to degrade adhesion. Also, H. Nakagawa et al. have said that decreasing solute Ti is effective to good adhesion. This estimation is based on SEM micrographs of pretreated Ti-IF steel. They mention that only grain boundaries are deeply etched when solute Ti exists, and that uneven etched surface is related to the deterioration of adhesion. The existence of “solute Ti” means both “interstitial-free” and “the existence of many precipitates”. Regardless of Ti addition, when the purity of steel is high and solute carbon and nitrogen are stabilized with alloy elements, grain boundaries are always deeply etched. Since no IF steel for porcelain enamel exists except for Ti-IF steel, we can not say whether their estimation is consistent with our results or not. However, reducing “solute Ti” means that the amount of Ti-related precipitates, including TiS, is lowered. Some parts of their speculation are similar to ours.

Although no proofs have been directly shown in Ref. 7, it is similar with our concept to explain the deterioration of adhesion by using that “increment of smut by increment of Ti addition”. According to our data, the increment is presumed to be TiS.

Also, the deterioration of adhesion at the repetition of firing in Ti-IF steel should be discussed along the theory to degrade its adhesion at one firing. These two phenomena should have the same root. We presume that TiS-related reaction to steel and enamel layer worsens adhesion, and the tendency proceeds as firing is repeated.

Based upon this theory, when we use steel sheet with TiS as a precipitate and it is pickled over a certain level, its adhesion will get worse.

5. Conclusions

We studied the adhesion in Ti-IF steel for porcelain enamel at the repeated firing. In Japan, highly-concentrated H2SO4 is accepted in pickling process and also its process line speed can not be lowered only for Ti-IF steel. Therefore, under the above conditions, the following results are obtained to keep good adhesion.

(1) The origin to deteriorate adhesion is presumed to be “TiS” on pretreated Ti-IF steel for porcelain enamel. Reduction of TiS is effective to keep good adhesion even at the 4th repetition of firing.

(2) Decreasing TiS corresponds to low pickling properties. When evaluated with pickling loss weight, it should be below 30 g/m2 to lower TiS in order to keep satisfactory adhesion.

(3) Under typical pretreatment conditions in Japan, it is effective to lower pickling loss weight (reducing the quantity of TiS in the smut) by adding Cu and lowering P. In order to keep good adhesion at repeated firings in severe pretreatment such as at 78°C for 4 min with 17% H2SO4, Cu should be higher than about 0.04% and P should be lower than about 0.013%, and by the optimization of Cu and P, pickling weight loss should be below 30 g/m2.

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