FULL PAPER

Compositional dependence of structure and wetting properties of CoO-doped silicate glass for porcelain enamel

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In this study, we investigated the relationship between the structural changes and wetting properties of porcelain enamel doped with CoO. Glass with the composition $45\text{SiO}_2\text{--}15\text{B}_2\text{O}_5\text{--}25\text{NaO--}15\text{CaO}$ was doped with different CoO concentrations. The wetting properties were characterized by high-temperature microscopy and the structural changes were observed by scanning electron microscopy, X-ray photoelectron spectroscopy, electron probe microanalysis, Fourier transform infrared spectroscopy, and energy dispersive X-ray spectroscopy. CoO addition increased the number of non-bridging oxygen atoms in the glass system, as well as the wetting ability. The addition of CoO to the porcelain enamel not only increased adherence, but also decreased the sintering temperature.

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Key-words : Enamel, Co-Fe, Wetting property, Structural Change

[Received February 14, 2018; Accepted March 27, 2018]

1. Introduction

Enamels are thin layers of glass on metal substrates. Many studies have investigated the adhesion of enamels to steel plates. Enamels are primarily used to coat metals such as gold, silver, and copper.¹⁾ Enamel coatings commonly comprise two layers. The first layer adheres to the metal body and the second cover layer enhances the appearance of the piece and protects its properties.^{2),3)} Recently, single-layer enameling has become more popular in the production of architectural parts and chemical reactors, gradually displacing two-layer enameling because of the decreased number of applications and firings required for fabrication.^{4),5)} Therefore, single-layer enamels must be defect-free in order to provide simultaneous chemical durability and adhesion ability.

Many previous reports on this topic have described theoretical models of the adhesion between enamel and steel. In a mechanical model, a rough interface is required for strong adherence because it enables mechanical anchoring. The rough surface is obtained by chemical corrosion and dendrite growth upon firing.^{6)–8)} In a chemical model, direct atomic bonds must be formed in an intermediate oxide layer between the metallic bonds of the substrate metal and the ionic bonds of the enamel.^{9),10)} Ni,¹¹⁾ Co,^{12),13)} and Ti¹³⁾ are commonly used to improve adherence, but the doping of enamel with Co has been observed to be more effective than that with Ni or Ti.^{13),14)}

The aim of the present study is to investigate the effect of the addition of Co on the adherence property of single-

layer enamel using high-temperature microscopy and on the enamel structural changes using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA), Fourier-transform infrared spectroscopy (FTIR), and energy dispersive X-ray spectroscopy (EDX).

2. Experimental method

The chemical composition of the enamel frit is $45\text{SiO}_2\text{--}15\text{B}_2\text{O}_3\text{--}25\text{Na}_2\text{O--}15\text{CaO--}x\text{CoO}$ ($x = 0, 2, 4$, and $6 \text{ wt } \%$). All materials were purchased from Junsei Chemical Co. (Tokyo, Japan) and batches were mixed by continuous grinding for homogenization. The mixed batches were melted at 1350°C for 1 h. The molten glass was then quenched on a stainless steel plate. The obtained glasses were annealed at the glass transition temperature, T_g , for 1 h, cut, and mechanically polished to obtain samples for thermal analysis. The thermal properties of the glasses were investigated using a thermal mechanical analyzer (Q400, TA Instruments) in the range from room temperature to 610°C with the heating rate of $10^\circ\text{C}/\text{min}$. The thermal property values were determined for each glass using the associated computer software; the accuracy of the measurements was $\pm 2^\circ\text{C}$, based on the average of three replicates.

The enamel frit was manufactured using a typical procedure after milling to 200 mesh. Sheets of steel (POSCO, Korea, C < 0.08%) were treated to remove all surface oils and rust for use as the enamel substrate. The all-enamel slip was manually coated on $10 \times 10 \text{ cm}$ steel plates using a spray gun, creating layers with an average thickness of approximately $150 \mu\text{m}$ (equal to 4–6 g). The coated plates

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were dried at 200°C for 10 min and then fired in a box furnace at 800, 850, and 900°C for 10 min.

To understand the microstructure of the enameled steels produced with different CoO amounts, cross-sectional specimens were prepared by a standard metallography procedure. The interfacial microstructure was examined using SEM (SUPRA40VP, ZEISS). The microscope was operated at an accelerating voltage of 20 kV. The elements in the glass/steel interface were chemically analyzed using an EDX system on the SEM. EPMA (SX100, Cameca) was employed to study the details of the interfacial reactions between the enamel coating and the steel substrate.

XPS was employed to analyze the changes in bridging and non-bridging oxygen atoms in the glass. XPS measurements were performed using ESCALAB250 XPS and Theta Probe XPS systems using monochromatic AlK α ($h\nu = 1486.6$ eV) radiation conditions. The analysis area was 400 μm and the data was compensated using C 1s (284.6 eV) as the reference. With a good signal-to-noise ratio, errors in the peak positions are ± 0.2 eV.

In order to observe partial structure changes, attenuated total reflectance (ATR) FTIR ATR-FTIR (Nicolet™ iN™10 Infrared Microscope, Thermo Scientific) measurements of the samples were performed. A square aperture of 30 $\times$ 30 μm was set parallel to the enamel/substrate interface. The square aperture was moved from the glass to the substrate for measurement. A series of FTIR spectra were recorded with a resolution of 4 cm^{-1} .

Contact angle measurements were performed on the glass samples using an automatic hot-stage microscope (HSM, H. Lab Co, Korea). The measurement was performed in air at the heating rate of 10 °C/min. The samples for these measurements were made using a hand press to compress 0.1 g of the glass frits, which were placed within a small cylindrical metal mold (10 $\times$ 10 mm). A sample image automatically recorded and analyzed the sample geometry during heating process. An alumina plate (20 $\times$ 20 $\times$ 0.7 mm) was used as the substrate.

3. Results and discussion

Figure 1 shows SEM images of the interface between the enamel and steel. In the case with no CoO in the enamel glass, the precipitation of the micro-alloy is lacking, which results in a smooth interface without dendrites [Fig. 1(a)], but the CoO-doped samples show dendritic structures [Figs. 1(b)–1(d)].

Dietzel^{15)–18)} reported an electrochemical reaction of Co and Fe that promoted adherence. Herein, Fe dissolves locally and causes significant roughening. Because of the deposition of Co and the selective dissolution of Fe, dendrite-like structures were observed. King et al.¹⁸⁾ showed that the dissolution of the Fe oxide layer was enhanced in the presence of Co. After the dissolution of the oxide layer, Co in the enamel reacts with Fe. In particular, some of the ferrous Fe is assumed to undergo a disproportionation reaction yielding ferric and metallic Fe, respectively, and the latter alloys with the reduced Co metals. Thus, it is assumed that the overall reaction is as follows:¹⁹⁾

Interfacial reactions among Co, enamel, and steel produce many small islands on the steel substrate. From the SEM micrograph of Fig. 1, it can be seen that the islands are interconnected to form anchor points, thus increasing the roughness of the interface. Similar improvements of the adherence of the enamel to steel by mechanical interlocking have been reported by other investigators.^{20),21)}

In order to confirm the Fe–Co composition, EPMA was used to investigate the distribution of Fe and Co at the enamel/steel interface. **Figure 2** shows the EPMA elemental maps of Fe and Co across the interface after heating at 850 and 900°C. As is shown in Fig. 2, an obvious Fe–Co dendrite is formed at the interface between the steel and glass enamel.

Fig. 1. SEM images of enamel/steel interface: (a) 0 wt % CoO at 850°C, (b) 2 wt % CoO at 850°C, (c) 4 wt % CoO at 850°C, and (d) 4 wt % CoO at 900°C. Dotted circles indicate dendrite structures.

Fig. 2. EPMA image of interface between enamel and steel: (a) Co mapping of 4 wt % CoO at 850°C, (b) Fe mapping of 4 wt % CoO at 850°C, (c) Co mapping of 4 wt % CoO at 900°C, and (d) Fe mapping of 4 wt % CoO at 900°C.

Fig. 3. High-resolution O 1s core-level photoelectron spectra for (a) 0 wt % CoO, (b) 2 wt % CoO, (c) 4 wt % CoO, and (d) 6 wt % CoO.

Figure 3 shows the O 1s core-level XPS peaks. The O 1s spectra of the obtained glasses use Shirley backgrounds and Lorentzian–Gaussian line shapes. Based on O 1s peak deconvolution with two contributions, the ratio between the number of non-bridging oxygen (NBO) and the total number of oxygen atoms was determined. The lower binding energy peak at 529.6 ± 0.2 eV is associated with NBO and the higher energy peak at 530.4 ± 0.2 eV with the bridging oxygen (BO).²²⁾ The results of fitting the experimental O 1s spectra show that the BO/NBO ratio decreases as the Co content increases.²³⁾ The O 1s spectra are fitted with contributions from both BO and NBO; the NBO signal increases with increases in the CoO content, indicating that Co behaves as a network modifier.

Figure 4 shows the FTIR spectra of the base and Co-doped glass heated at each temperature in the range of $700\text{--}1600\text{ cm}^{-1}$. As seen in the right-hand SEM image,

Fig. 4. FTIR spectra according to each position as a function of CoO contents: (a) 0 wt % CoO at 850°C, (b) 4 wt % at 850°C, and (c) 4 wt % at 900°C.

Fig. 5. Elemental distribution in cross-sections of enamel/steel plane of each specimen by EDX: (a) 4 wt % Co at 850°C and (b) 4 wt % at 900°C.

the measurement point (a) in the SEM image is far from the enamel/steel interface while (c) is near the interface. All the samples show similar trends; the FTIR spectral bands of all glasses confirm the main characteristics of the silicate network, possibly due to the presence of SiO_2 as a major constituent. The major band at approximately 1028 cm^{-1} can be attributed to Si–O–Si stretching. The small band at 1400 cm^{-1} can be attributed to the C–O vibration mode. The intensity of the peak is increased as the concentration of CoO increases, which is attributed to the breaking of the Si–O–Si network.²⁴⁾ The intensity of the band increases with CoO addition to the base glass; therefore, the CoO increases the NBO in the network. Although differences in the C–O peak at each measured point are not well observed from the 850°C sample in Fig. 4(b), the intensity of the C–O peak is increased near the enamel/steel interface in the 950°C sample in Fig. 4(c), which may arise from the Co–Fe reaction depending on the temperature.

The temperature dependency of structural change also appears in the EDX results (Fig. 5). The EDX line scan across the interface shows that, with increasing temperature, the fraction of Co changes in the enamel. In the sample heat-treated at 900°C, the decrease of Co is longer than that in the 850°C sample.

The effect of adding CoO on the thermal properties of the glasses is shown in Fig. 6. The thermal properties of the glasses are correlated with their compositions and structures. A monotonic change occurs in the glass transition temperature, T_g , and the dilatometric softening temperature, T_d . The T_g value decreases with increasing CoO, from 565.1 to 550.2°C as the CoO amount increases from 0 to 6 wt %. The T_d value also decreases with increases in CoO from 0 to 6 wt %, from 602.4 to 588.3°C. Figure 6 also shows the effects of the Co amount on the coefficient of thermal expansion (CTE) of the glasses. The CTE of the glasses increases with increasing Co content, from 89.4×10^{-7} to $92.4 \times 10^{-7}\text{ K}^{-1}$. Therefore, the increase in CTE and the decrease in T_g and T_d with increasing Co content may be attributed to the increase in the NBO content.²⁵⁾

Good wettability is among the most important factors influencing favorable adhesion. The pellet shape of the glass with increasing CoO amount is depicted in Fig. 7;

Fig. 6. Thermal properties of CoO-doped glass as a function of CoO contents.

the pellets are initially cubic in shape (Region I). With increasing CoO amount, the pellet shape changes from cubic to spherical. The formation temperature of the swollen sphere is known as the softening point, T_s . Heat energy first affects the corners because they have the largest surface area. Therefore, the corners of the pellet contract rapidly to reduce the surface energy.²⁶⁾ At the higher temperatures ($>T_s$), the shape of the pellet changes to ellipsoidal (Region II) and the molten glass spreads over the substrate (Region III).

The wetting behaviors of the glasses on the low-carbon steel substrate were studied according to the CoO amount, as shown in Fig. 8. The wetting angle of the 0 wt % CoO glass was maintained from room temperature to 750°C. Above 750°C, the glass begins to wet the substrate. As the amount of CoO increases, the starting temperature of the swollen sphere is decreased (Figs. 7 and 8). In this study, the wetting behaviors of the glasses containing 6 wt % CoO are better than that of the glass with 0 wt % CoO. Furthermore, the addition of higher amounts of CoO improves the wettability of the glass on the substrate at the same temperature. At 950°C, the value of the wetting angle of the 6 wt % CoO composition is approximately 62.8°. This phenomenon is closely related to the glass structure. As shown in the XPS and FTIR analyses, adding CoO changes BO into NBO. Consequently, the glass

Fig. 7. Heat reaction of CoO-doped glass pellets on a substrate. (a) 0 wt % CoO, (b) 2 wt % CoO, (c) 4 wt % CoO, and (d) 6 wt % CoO.

Fig. 8. Wetting angle of CoO-doped glasses as a function of temperature for various CoO contents.

network is weakened and the glass flows more easily, which improves the glass wettability.

4. Conclusions

In this study, the effects on the structure and wetting ability according to the amount of CoO in enamel were studied. CoO addition induces dendritic structures at the enamel/steel interface and improves the adherence of the enamel to steel by mechanical interlocking.

Regarding the structural changes, CoO functioned as a network modifier, increasing the amount of NBO as CoO was added to the glass structure. The thermal properties such as T_g and T_d are related to the glass structure; these characteristic temperatures were also decreased with increasing CoO amounts in the glasses.

Adding CoO increased the wetting ability of the enamel. The glass with 6 wt % CoO shows the best wetting ability among the samples, with the wetting angle of 62.8°.

Acknowledgement This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea.

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