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Physiochemical Effects of SiC and ZrO₂ Particle Fillers on the Properties of Enamel Coatings

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Abstract: The ceramic particles of SiC and ZrO₂ are embedded as fillers in the enamel coating with varying contents of 0.03, 0.05, and 0.1 wt %, and the surface properties are measured. It is found that the addition of ceramic fillers indeed causes changes in surface properties. The roughness was influenced mainly by the particle size embedded. The contact angle decreased at 0.03 and 0.05 wt % and equivalent to that of no filler at 0.10%. Our analysis suggested that the contact angle is influenced by both surface roughness and surface morphology (with chemical composition). The microstructure and elemental analysis suggest that the chemical composition and shape of Al, Ce, Ca, and P-rich aggregates on the enamel surface are showing significant changes when fillers are added. It is observed that the Al- and Ce-rich aggregates decrease both in number and size as the filler content increases, and Ca-rich aggregates change their shape from needle to spot at 0.1 wt % inclusion. The washability is notably improved at 0.1 wt %, which corresponds to the content where the drastic microstructure change occurred. The examination of the contaminated surface revealed that the phosphate component in the contamination has reacted with the Ca-rich phase of the needle-shape during the process of burning, thus inhibiting an easy removal of the contamination. Therefore, the formation of the Ca-rich phase of the needle-shape on the enamel surface should be suppressed for easy-cleaning enamel coatings for cooking wares.

Keywords: enamel; coatings; ceramic filler; SiC; ZrO₂; washability

1. Introduction

Vitreous enamel coating is a substantially glassy inorganic coating applied to a metal substrate by thermal fusion. It has good abrasion, wear, and chemical resistance, high hardness, various colors, and incombustibility. While the properties of the vitreous enamel are closely related to the properties of its components, these properties can be controlled by tailoring the composition [1–3], microstructure [4–6], and crystallization of the coating [7–9]. One of the aspects desired for the enamel coating is the non-stick coating or easy-cleaning coating to easily detach the burned contamination in the high-temperature cooking apparatus, such as the gas or electric ovens. While there are a number of patents and articles [10–12] on the durability of enamel coatings, especially on the abrasion [2,3,13,14] and corrosion resistance [2,6,7,15–17], less is understood how the surface microstructural features of enamel scales influence the washability.

For the easy-cleaning enamel coatings, there are an array of self-cleaning coatings on the industry that are typically categorized into two types depending on the cleaning mechanism: catalytic and

pyrolytic. The catalytic-enamel coating has a porous structure where these pores can absorb the burned contamination, and the catalytic substances like metal oxides in the enamel coating help the decomposition of foods into carbon dioxides and water. During this cleaning cycle, the product is heated to 200 °C or higher to burn off and soften excess grease deposits. One can then simply wipe away any residue with some soapy water. The pyrolytic-enamel cleans by elevating the temperature to an extreme degree over 500 °C. The heat reduces the baked crust and grease to powders, which are easily removed. Since the process creates smoke and fumes, some pyrolytic-cleaning coatings are provided in a hybrid type containing catalytic components.

Nevertheless, there are several issues associated with both types of catalytic- and pyrolytic-enamels. The lifespan and hardness are limited due to the porosity in the structure, and the increase of energy index due to high-temperature cleaning as well as the production of ashes. Therefore, there still are needs for the development of an easy-cleaning enamel that is durable and cleansable at not even high temperatures.

Incorporation of additives in the coating is a well-known method to introduce both microstructural change and surface chemistry, which can alter the repellence to undesired matters, such as water and impurities [18]. One could introduce a secondary substance to modify the crystallography and morphology of the enamel scale [19,20]. For instance, the addition of Al_2O_3 in the enamel improves the hardness of the coating but also induces the formation of a fine-grained enamel coating [21], thus altering the microstructure. Rossi et al. [22] showed that the presence of the micro- Al_2O_3 particles improved the abrasion resistance of the enamel coating, which resulted in limited corrosion resistance. Likewise, the crystal distribution and surface chemistry can be tailored by controlling contents.

In the present study, ceramic particles are incorporated into the enamel coatings to induce physiochemical changes such as surface roughness, chemical reactivity, and morphology. We focused on (i) how the surface properties of enamel coatings incorporated with ceramic particles are modified when SiC and ZrO_2 particles are utilized as ceramic fillers, and (ii) how these changes influence the washability.

2. Experimental Details

2.1. Preparation of Enamel Coating

Enamels are silicate-based materials that are deposited by a spray gun then fused at high temperatures. A commercially-available alkali borosilicate glass frit from Hae Kwang enamel coating Co. Ltd. was used. The composition of frits is designed for easy-cleaning coatings for cooking wares [23–25]. In Table 1, the chemical composition of enamel frit from inductively coupled plasma (ICP) results is shown. Firstly, raw materials of glass frits and clay (kaolin) were ball-milled to achieve homogenized powders. For SiC or ZrO_2 filler-added cases, fillers were ball-milled together at this stage with glass frits and clay. The powders were sieved with 180 μm of mesh, and the average size of sieved particles was 30–40 μm . The enamel slurry was prepared by mixing powders in the water to provide a stable suspension. The enamel slurry without filler was used as a reference enamel coating, which will henceforth be referred to as NF.

The contents of SiC and ZrO_2 particles were set to be 0.03%, 0.05%, 0.1%, and 0.2%, and this is given in Table 2 along with the particle information. The field emission scanning electron microscopy (FESEM) images of SiC and ZrO_2 particles are shown in Figure 1. The SiC and ZrO_2 particles were chosen as reprehensive non-oxide and oxide ceramic fillers, and their high melting point makes them suitable for investigating their physiochemical effects. A particle size between 0.5 and 3 μm was chosen to induce an effect on surface roughness. For SiC, micron-grade was chosen as nano-grade can undergo surface oxidation during the oxidation. The change to SiO_2 on its surface may undermine the generic effect of SiC, which is against our initial intention. It should be noted that there is a difference in number density (i.e., spatial distribution) for two cases that may have influenced the changes in observed aggregates. However, the effect by their presence will be confirmed later in this paper, and the difference in the number density does not change our major conclusions.

For the substrate, a cold-rolled steel plate of 0.8–1 mm thickness and 100 × 150 mm in size was used. Before coating, all plates were sand-blasted and cleaned with a commercially-available cleansing solvent. The cleaned plate was sprayed with a prepared slurry and fired at 840 °C for 5 min, then finally cooled to room temperature. The firing treatment at high temperature melted the glass frit and chemically bonded the enamel to the steel. During enameling, the plates were loaded in the furnace. The final thickness of the enamel scale was measured as 135 ± 15 µm.

Table 1. Chemical composition analysis of enamel used in this study.

Components	Contents (wt %)
SiO ₂	55.4
Na ₂ O	14.9
B ₂ O ₃	14.8
TiO ₂	2.87
NiO	2.66
Al ₂ O ₃	1.8
SrO	1.37
Li ₂ O	1.06
K ₂ O	0.98

Table 2. Ceramic fillers used in the study and their fundamental properties.

Filler	Manufacturer	Particle Diameter (µm)	BET (m ² /g)
SiC	Sinxing Advanced Material Ltd. (Hongkong, China)	2.61 ± 1.68	3.17
ZrO ₂	Sinocera (Shandong, China)	0.51 ± 0.38	9.07

Figure 1. FESEM images of (a) SiC and (b) ZrO₂ particles.

2.2. Evaluation of Enamel Coating Properties

As the homogeneity can be an issue in evaluating surface properties of sprayed enamel coatings, multiple locations of three specimens of identical conditions were subjected to the measurements.

The surface roughness of the scale was assessed using a laser microscope, OPTELICS (Lasertec, Yokohama, Japan). For the measurement, three specimens were prepared for each condition (by filler type and content), and the surface roughness was measured at 25 different positions of each specimen. To evaluate the surface roughness of the enamel scale, we introduced the roughness average, R_a . The roughness average is the arithmetic average of the absolute values of the profile heights over the evaluation length, which can be expressed in the equation (Equation (1)) as:

$$R_a = \left(\frac{1}{L}\right) \int_0^L |z(x)| dx \quad (1)$$

where L is the evaluation length, x is each of measured points on the evaluation length, and $z(x)$ is the profile height function.

The contact angle of water on the enamel coatings was directly measured on the coating surface of the steel substrate using Phoenix 300 ET goniometer (Surface Electro Optics, Suwon, Korea). A syringe with a 2 mm inner diameter was used to supply liquid into the sessile drop from above the sample. A sessile drop was about 6–8 μm^3 in volume and 0.1–0.2 cm in diameter at room temperature. The three-phase contact line of the droplet was then drawn automatically by computer. The above procedures were measured for fifteen drops on the new surfaces of a single specimen and repeated on a total of three specimens. All readings were then averaged for each condition.

The microstructure and the elemental analysis of the coatings were performed by means of field emission scanning electron microscopy (FESEM, JSM 7610F, JEOL, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS).

2.3. Contamination on Enamel Coating and Cleaning Test

The burnt contamination is applied on the enamel coating using a mixture of foods, which are specified in Table 3. The 1g mixture of food was pasted on a 50 mm $\times$ 70 mm area on the enamel scale. The pasted enamel plate was kept in a 250 $^{\circ}\text{C}$ electric oven for one hour, then cooled down to room temperature. The entirely cooled down samples, Figure 2a, were then immersed in 60 $^{\circ}\text{C}$ water for 30 mins. For the cleaning test of burnt contamination, an abrasion rubbing tester (KP-M4250, KIPAE Ent., Suwon, Korea) was utilized, where a constant force was exerted on the sample surface while the sample moved back and forth in horizontal directions. A 60 $\times$ 60 mm non-scratch scouring pad was attached on the equivalent size of the steel plate to aid homogenize the exerted forces, as shown in Figure 2b. The sample was fixed on the abrasion testing machine and a 2 kg weight was added on top of the axial bar. The cleaning test was performed by having the axis traveling 10 cm back and forth over the contaminated area for 50 cycles, followed by a wash-out of debris with flowing water. The specimen was then dried for 10 mins in a 100 $^{\circ}\text{C}$ electric oven.

Table 3. List of food and weight used for burnt contamination test.

Contents	Quantity	Units
Cherry (Canister)	200	mL
Tomato juice	200	mL
Egg (yolk)	6-7	Counts
Milk (2%)	112	g
Tapioca (powder)	5	g
Pork fat	112	g
Cheese	112	g

Figure 2. Optical images of (a) enamel-coated steel substrate after burnt contamination treatment and (b) experimental settings for washability test.

The washability was then calculated by the following equation (Equation (2)), which essentially is the weight portion of contamination removed divided by the weight of contamination initially applied:

$$\text{Washability (\%)} = \frac{([W_1 - W_0] - [W_2 - W_0])}{W_1 - W_0} \times 100 \quad (2)$$

where W_0 is the weight of as-coated specimen and W_1 is the weight of specimen after burning the food on top of as-coated (burnt contamination). The W_2 is the total weight of the test specimen after the cleaning test.

3. Results and Discussions

3.1. Changes in the Fundamental Surface Properties

3.1.1. Roughness

Figure 3a shows the result of measuring the surface roughness value, R_a , by filler contents. The effect of substrate roughness on the measured R_a values are neglected because the highly viscous enamel slurry forms a fairly uniform net-thickness of 135 μm , and this thickness is much greater than the surface roughness of the substrate ($R_a = 2.9\text{--}3.2 \mu\text{m}$). For NF, R_a was measured as 1.7 μm . The R_a value of the SiC-added sample did not change significantly in the 0.03 and 0.05 wt % contents but increased to 2.1 μm at the 0.1% content, which is approximately 25% augmentation compared to the NF. On the other hand, ZrO_2 -added samples showed a slight increase in R_a value at 0.03 wt %, and a minute decrease at 0.05 and 0.1 wt % compared to NF.

The particle size of the frit powder used in this work is within range of 30–40 μm , which was melted and sintered during the spraying process, resulting in approximately a 135 μm -thick enamel scale. The melting points of bulk SiC and ZrO_2 are 2830 and 1855 $^\circ\text{C}$ [26], respectively, which are embedded in the enamel without any melting during the coating process. For SiC fillers, the average particle size is 2.3 μm , and it appears that the relatively large SiC particles are encompassed by the enamel coating, causing an effective increase in roughness when the content is sufficiently high (in this case, 0.10 wt %). In contrast, ZrO_2 , whose average particle size is 510 nm, has no significant effect on roughness for 0.03–0.10 wt %. The small particles are expected to settle in the free volume between the large enamel particles. Furthermore, the roughness of NF (i.e., no filler) is greater than its size. For these reasons, the effect of such sub-micron particles on the contact angle is considered to be negligible. As a matter of fact, the studs of SiC composition were observed on the surface (Supplementary Materials S4), whereas none observed were for ZrO_2 in the later results of element mapping via energy-dispersive spectroscopy (not shown in Supplementary Materials as none detected).

3.1.2. Contact Angle

The contact angle is a method of confirming the hydrophilicity of the surface, and when the contact angle is high, the cleaning ability of the surface may be superior to that otherwise. Figure 3b shows the contact angle results of the enamel surface with SiC and ZrO_2 fillers. In the case of SiC, the lowest contact angle was observed at 0.03 wt % content. At 0.05 and 0.1 wt %, the contact angle increased as the content increased. For ZrO_2 , the contact angle decreased as the content increased at 0.03% and 0.05%. It should be noted that the contact angle reduction is much greater than that of SiC at these contents. At 0.05%, the lowest contact angle was observed, and at 0.1%, a similar value compared to that of NF was observed.

Figure 3. (a) The surface roughness R_a and (b) water contact angle of the surface of enamel coatings with SiC/ZrO₂ fillers.

The roughness of the surface may have influenced the contact angle, as the water droplet size is approximately 100 μm , so the micron-scale roughness can play a role. For the contact angles of SiC, a similar relationship was observed for the roughness. It seems that the roughness of the surface have influenced R_a and the contact angle; they both decrease at low contents but increase at high contents. Yet, it is premature to conclude that the factor that affects the contact angle is merely roughness. In the case of ZrO₂, the roughness did not change significantly depending on the content, whereas the contact angle showed a similar tendency to SiC. In addition, considering that the roughness values of SiC and ZrO₂ at 0.03 and 0.05 wt % are within statistical error, it is hard to explain the large decrease in contact angle observed in ZrO₂ alone. In summary, for both SiC and ZrO₂, the contact angles tended to decrease at 0.03% and 0.05% and increase at 0.1%, reaching an equivalent value compared to NF. The roughness of the enamel surface likely to play a role in contact angles measured, but it is expected there are other factors influencing the contact angles. The surface phase change induced by embedded ceramic particles, which will be later discussed in microstructural and elemental analysis, possibly influenced the contact angle as well.

3.2. Microstructural and Elemental Analysis

The microstructure of the enamel scale is observed by FESEM and EDS, and the results are summarized in Figures 4 and 5. In the EDS analysis, only the elements showed a correlation to surface morphology are presented, which are Al, Ce, Ca, and P.

For NF (0.00% of Figures 4a and 5b), aggregates for three elements are observed; Al, Ce, and Ca (P is presented to make comparison with later results in Section 3.4). Al- and Ce-rich aggregates were both in spot shapes with diameters approximately 1–4 and 3–7 μm , respectively. On the contrary, the Ca-rich aggregates were in a needle-shape with the dimension being approximately $0.5 \times 4 \mu\text{m}$. Since none of the elements with atomic number (Z) > 8 showed clear appearance with Ca-rich aggregates, it is reasonable to presume that these Ca-rich aggregates are compounds with light elements such as H, C, and O. In the further discussion, these aggregates will be notated as ‘X-phase’, where X is the element (e.g., Ca-phase). It is noteworthy that the distributions of Al and Ce/P elements were observed mutually exclusive (i.e., Al depleted in a Ce- and P-rich region, and vice versa), but the distribution of Ca element was found independent of Al, Ce, and P.

When ceramic fillers are added, the change in surface crystallography is observed, as illustrated in Figure 4. At SiC contents of 0.03%, the distribution of Al-phases increases in number while being equivalent in size. For Ce and Ca aggregates, the shape and number were similar to those observed in NF. When SiC contents are increased to 0.05%, both Al and Ce aggregates decreased both in size and number. Furthermore, in the case of Ca, the needle-shape phases were no longer observed. In SiC

0.1%, it can be seen that the number of Al and Ce aggregates decreased notably. Ca-phases were no longer in a needle-shape; they were in the spot shapes.

Figure 4. FESEM images and corresponding EDS analysis (Al, Ce, Ca, and P) for enamel-coated surface with the addition of SiC at (a) low and (b) high magnification.

As for ZrO_2 (Figure 5), a similar tendency was observed; the Al-phase and Ce-phase became smaller and less frequent as the filler content increased. On the contrary, the needle-shape Ca-phase appeared up to 0.05 wt % and diminished at 0.1 wt %. At 0.1 wt %, no visible needle-shape configuration is observed in the FESEM images, and EDS analysis also indicates that there is no clear Ca-rich phase with a high aspect ratio. Instead, they seemed to be in an intermediate state since the Ca-phases are found in either spot or short needle. It may be argued that the shape is changed, but there is also a possibility that the growth of the crystal is inhibited due to the presence of the fillers, and the crystal may exist in a small size.

With the observed changes in the surface chemistry, the contact angle change with respect to the filler contents can be further discussed. As stated in the previous section, changes in contact angles cannot be understood solely by roughness. Although the exact influencing chemical compositions cannot be identified, due to the experimental challenges, some implications can be drawn. When comparing 0.03% and 0.05% to NF, there is a significant increase in Al-phase and a decrease in the number density of Ce-phase. It can be inferred that the increased Al-phase and decreased Ce-phase contribute to decreasing the contact angle. At 0.1% SiC and ZrO_2 , the surface change (non-needle-shape Ca-phase such as spot-shape or none) may have increased the contact angle. These implications are yet

speculative, but more importantly, they provide a case that the surficial changes in crystallography might be determined by other properties such as contact angle.

From the microscopic and elemental analysis, it was confirmed that the distribution and shape of the crystal phases on the enamel surface depend on the content of ceramic filler. The addition of fillers not only cause the changes in roughness or suppression of crystal growth, but changes in local chemistry that completely alters surface crystallography. Moreover, drastic changes were observed at 0.1 wt %, where the Al and Ce phases decrease in both number and size, and the needle-shape Ca-phases are no longer observed.

Figure 5. FESEM images and corresponding EDS analysis (Al, Ce, Ca, and P) for enamel-coated surface with the addition of ZrO_2 at (a) low and (b) high magnification.

3.3. Washability of Enamel Coatings and Its Relation to Surface Properties

The effect of SiC and ZrO_2 particles on enamel washability is examined and summarized in Table 4 along with the previous roughness and contact angle results. In Figure 6, the results from the contamination cleaning test are shown. For both fillers, 0.03 and 0.05 wt % showed a minute decrease, or negligible change in washability compared to NF; for SiC (ZrO_2) contents of 0.03 and 0.05 wt %, 3.7% (2.8%), and 3.3% (5.4%), respectively. The difference in washability between NF and low contents (0.03 and 0.05 wt %) was within the statistical error. On the other hand, for 0.1 wt % of SiC and ZrO_2 , the washability increased by 16.3% and 21.3% compared to NF. It is obvious that the content beyond a certain amount indeed increases the washability.

Table 4. A summary of evaluated properties for ceramic filler (SiC or ZrO₂)-added enamel scales.

Filler Type	Contents (wt %)	Contact Angle (°)	Roughness, R _a (μm)	Washability (%)
No Filler (NF)	0.00	62.4 ± 2.7	1.67 ± 0.13	80.9 ± 2.1
SiC	0.03	52.8 ± 1.4	1.62 ± 0.13	77.9 ± 3.5
	0.05	55.6 ± 1.5	1.70 ± 0.20	78.2 ± 1.8
	0.10	64.0 ± 1.7	2.10 ± 0.20	94.1 ± 2.4
	0.10	64.0 ± 1.7	2.10 ± 0.20	94.1 ± 2.4
ZrO ₂	0.03	46.9 ± 4.4	1.81 ± 0.15	78.6 ± 4.7
	0.05	45.6 ± 2.1	1.45 ± 0.17	76.5 ± 8.0
	0.10	61.2 ± 2.8	1.55 ± 0.14	98.1 ± 1.0

Figure 6. The washability of burnt contamination on enamel coatings with different contents of SiC/ZrO₂ fillers.

Based on the previous results, the mechanism responsible for the change in the washability is expected to be a combined effect of roughness and surface chemistry. However, the mechanisms might be different for two fillers. For SiC additions, it is considered that roughness contributes to the increased washability when the filler is sufficiently added (about 0.1). The chemical composition change of the surface further affects the washability (needle-shape Ca-phase completely disappeared at 0.1 wt %). The ZrO₂ particles, whose particle size is an order smaller than SiC and two orders smaller than enamel powder, is simply sandwiched between enamel powders and show a minute change in surface roughness. Thus, in this case, the increased washability at 0.1 wt % is attributed to surface compositions produced or changed by the addition of ZrO₂. Therefore, in the case of SiC, both the morphology and the composition of the crystals on the surface have effects on the washability, and in the case of ZrO₂, the composition is more influential.

Interestingly, the 0.1 wt % content, which showed improved washabilities for both SiC and ZrO₂, is consistent with the filler content at which drastic changes occurred in the microstructure analysis. As the distribution of surface crystal phases changes with varying filler contents, one can conclude the following: the shape and composition of the crystals on the surface affect the easiness of washout of burnt contamination, which means that certain crystal phases have a higher chemical or mechanical coherency to burnt contamination than other crystal phases. In order to fortify the aforementioned statement, we further investigated the surface of enamel coating after fully removing the burnt contamination in the following section in order to support such effects of surface crystals discussed above.

3.4. Surface Change in Enamel Coating After Burnt Contamination Cleaning

To evaluate the coherency of burnt contamination on the enamel coatings, we have compared the surface morphology after wiping out the burnt contamination. An identical abrasion testing machine

used in the cleaning test is again used, with the increased number of cycles, 200 times. After the wipe-out, no visible residue of burnt contamination is observed. Then the surface microstructure is analyzed in the same manner as in Figure 7.

Figure 7. The surface of SiC 0.03 wt %-added enamel coating after the washability test. (a) FESEM image and (b) image overlaid with Al, Ce, Ca, and P. (c–f) elemental map of each element (Al, Ce, Ca, and P).

Similar to NF without burnt contamination, the needle-shape of Ca-phase is observed (circled in Figure 7e). However, a change in phosphate distribution is observed at the burnt contamination-removed region; phosphate is concentrated along with the distribution of Ca-phase, which was not the case for NF (Figure 4). This infers that the needle-shape of Ca-phase is attracted to phosphate during the burning process of contamination. Phosphate is prevalent in the daily diet, and of course, was included in the organ meat, milk, and eggs, which were used for the food contamination in this work. Therefore, the Ca-phase is believed to capture phosphate during the carbonization of contaminants. In Figure 8, an illustrative comparison is presented to depict how needle-shape and spot-shape Ca-phases react differently with the phosphate in the food paste. The phosphate can either form epitaxial crystal structures on top of the Ca-phase or growth on the Ca-phase, forming calcium phosphates such as hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$).

One hypothesis is that the Ca oxalate phases, whose decomposition temperature is approximately 200 °C, became chemically active during food burning at 250 °C then reacted with phosphates to form hydroxylapatite. The presence of carbon in the enamel scale is verified by comparing the carbon contents in NF coating to that in the original frit powder (Supplementary Material S7). In an attempt to understand the crystal structure for Ca-phase in the as-coated and after-contaminated regions, we proceeded with the XRD analysis. It is worth mentioning that the deconvoluting peaks of the multi-element polycrystalline phase and interpreting them is a challenge to achieve reliable results. The XRD results are presented in Supplementary Materials S8, although identifying the crystalline phases was difficult for such cases. Based on the EDS analysis, it is suggested that the Ca-phase before contamination (needle-shape) is calcium oxalate, and the phase becomes hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) after being exposed to high temperatures with plenty of phosphate sources. Albeit the crystal structures playing a role need to be identified in further studies, it clearly shows the ceramic filler altered the surface crystallography, which in turn affected the washability of enamel coatings. Given these points, the Ca-phase chemically attracts the phosphate during the contamination process and makes the removal of contamination difficult, thus the demoting growth of a specific phase (the needle-shape Ca-phase in the present study) might be useful to be considered as a design criterion for non-stick or easy-cleaning enamel coatings.

Figure 8. An illustration depicting the difference in the chemical reaction with phosphate (a) needle-shape and (b) spot-shape Ca-phases. The enamel scale (blue) The Ca-phases are represented with red, and the phosphate distribution is shown with white color. (a) Phosphates are distributed along the Ca-phases; (b) phosphates are distributed independently from the Ca-phases.

4. Conclusions

The ceramic particles of SiC and ZrO₂ are embedded as fillers in the enamel coating with varying the contents of 0.03, 0.05 and 0.1 wt % to investigate the effect of ceramic fillers on the surficial properties and further impact on the washability. The following are the key conclusions from the present work.

- The presence of SiC/ZrO₂ filler not only changes surface roughness but also changes the surface crystallography, which in turn influences the contact angle and washability.
- For the enamel powers with sizes of 30–40 μm , 3 μm SiC powders increase the surface roughness when sufficient amount is added. In contrast, a small powder of 500 nm ZrO₂ infiltrates the voids between enamel powders and causes a negligible change in the roughness.
- The contact angle is affected by the roughness and the chemical composition of the surface. Both roughness and chemical composition played a role for SiC, while only chemical composition played a major role for ZrO₂.
- Both roughness and morphology of the surface are responsible for the change in the washability. The washability is notably augmented at 0.1 wt %, which corresponds to the content where the drastic microstructure change (and the contact angle) occurred.
- The changes in the surface crystallography are observed with the presence of the fillers. Al, Ce, Ca, and P aggregates showed significant changes (see main text for each change).
- The Ca aggregates was observed in a needle-shape in NF and 0.03–0.05 wt %. This phase is reactive with phosphates in the contamination during the firing process and makes the removal of contamination more difficult.

Throughout this study, the results presented in this paper can provide a useful guide in designing an easy-cleaning enamel coating. The washability is notably augmented when the fillers are added more than a particular amount (in our study 0.1 wt %), where a drastic microstructure change occurred. A drastic change can be verified by EDS analysis methods presented in this study, but also might be guided by measuring roughness and contact angles which are relatively less time- and cost-consuming methods. In addition, we have identified a certain phase (needle-shape Ca-phases in this work) impedes removal of the contamination. Suppression of such crystal formation needs to be considered for easy-cleaning enamel coatings.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/10/2/121/s1>.

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References

- Rossi, S.; Parziani, N.; Zanella, C. Abrasion resistance of vitreous enamel coatings in function of frit composition and particles presence. *Wear* **2015**, *332*–333, 702–709. [\[CrossRef\]](#)
- Rossi, S.; Scrinzi, E. Evaluation of the abrasion resistance of enamel coatings. *Chem. Eng. Process. Process Intensif.* **2013**, *68*, 74–80. [\[CrossRef\]](#)
- Scrinzi, E.; Rossi, S. The aesthetic and functional properties of enamel coatings on steel. *Mater. Des.* **2010**, *31*, 4138–4146.
- Yang, H.; Chen, C.; Sun, H.; Lu, H.; Hu, X. Influence of heat-treatment schedule on crystallization and microstructure of bauxite tailing glass–ceramics coated on tiles. *J. Mater. Process. Technol.* **2008**, *197*, 206–211. [\[CrossRef\]](#)
- Kim, M.T.; Chang, S.Y.; Won, J.B.; Park, H.W. Effect of hot isostatic pressing on the microstructure and mechanical properties of vitreous enamel coatings on low carbon steel. *Surf. Coat. Technol.* **2006**, *201*, 3281–3288. [\[CrossRef\]](#)
- Tang, F.; Chen, G.; Volz, J.S.; Brow, R.K.; Koenigstein, M. Microstructure and corrosion resistance of enamel coatings applied to smooth reinforcing steel. *Constr. Build. Mater.* **2012**, *35*, 376–384. [\[CrossRef\]](#)
- Wang, D. Effect of crystallization on the property of hard enamel coating on steel substrate. *Appl. Surf. Sci.* **2009**, *255*, 4640–4645. [\[CrossRef\]](#)
- Shao, H.; Liang, K.; Zhou, F.; Wang, G.; Hu, A. Microstructure and mechanical properties of MgO–Al₂O₃–SiO₂–TiO₂ glass–ceramics. *Mater. Res. Bull.* **2005**, *40*, 499–506. [\[CrossRef\]](#)
- Tkalcec, E.; Kurajica, S.; Ivankovic, H. Crystallization behavior and microstructure of powdered and bulk ZnO–Al₂O₃–SiO₂ glass-ceramics. *J. Non-Cryst. Solids* **2005**, *351*, 149–157. [\[CrossRef\]](#)
- Le Bris, S.; Dubanchet, A.; Perillon, J.-L. Cooking Item Comprising a Non-Stick coating with Improved Properties of Adhesion to the Substrate. U.S. Patent 9,199,275, 6 August 2013.
- Mostefa'i, M.; Auriac, Y.; Shanahan, M.E.R.; Bressan, J.; Meslif, A. Use of fluoroalkylsilanes as non-stick coatings for thermal by-products of linoleic acid. *Int. J. Adhes. Adhes.* **2000**, *20*, 257–261. [\[CrossRef\]](#)
- Rossi, S.; Gai, G.; De Benedett, R. Functional and perceptive aspects of non-stick coatings for cookware. *Mater. Des.* **2014**, *53*, 782–790. [\[CrossRef\]](#)
- Rossi, S.; Zanella, C.; Sommerhuber, R. Influence of mill additives on vitreous enamel properties. *Mater. Des.* **2014**, *55*, 880–887. [\[CrossRef\]](#)
- Ryabova, A.V.; Es'kova, T.A.; Karandashova, N.S.; Yatsenko, E.A.; Smolii, V.A. Development of a Method for Improving the Performance Properties of Glass-Enamel Coatings for Steel. *Glass Ceram.* **2015**, *71*, 327–329. [\[CrossRef\]](#)
- Tang, F.; Chen, G.; Brow, R.K.; Volz, J.S.; Koenigstein, M.L. Corrosion resistance and mechanism of steel rebar coated with three types of enamel. *Corros. Sci.* **2012**, *59*, 157–168. [\[CrossRef\]](#)
- Tang, F.; Chen, G.; Volz, J.S.; Brow, R.K.; Koenigstein, M.L. Cement-modified enamel coating for enhanced corrosion resistance of steel reinforcing bars. *Cem. Concr. Compos.* **2013**, *35*, 171–180. [\[CrossRef\]](#)
- Tang, Z.; Wang, F.; Wu, W. Effect of Al₂O₃ and enamel coatings on 900 °C oxidation and hot corrosion behaviors of gamma-TiAl. *Mater. Sci. Eng. A* **2000**, *276*, 70–75. [\[CrossRef\]](#)
- TÜRKÜN, M.; Sevgican, F.; Pehlivan, Y.; Aktener, B.O. Effects of 10% carbamide peroxide on the enamel surface morphology: A scanning electron microscopy study. *J. Esthet. Restor. Dent.* **2002**, *14*, 238–244. [\[CrossRef\]](#)
- Ling, G.; He, J. The influence of nano-Al₂O₃ additive on the adhesion between enamel and steel substrate. *Mater. Sci. Eng. A* **2004**, *379*, 432–436. [\[CrossRef\]](#)
- Rashwan, M.; Cattell, M.J.; Hill, R.G. The effect of barium content on the crystallization and microhardness of barium fluormica glass-ceramics. *J. Eur. Ceram. Soc.* **2019**, *39*, 2559–2565. [\[CrossRef\]](#)
- Goel, A.; Tulyaganov, D.U.; Agathopoulos, S.; Ferreira, J.M.F. The effect of Al₂O₃ on sintering and crystallization of MgSiO₃-based glass-powder compacts. *Ceram. Int.* **2008**, *34*, 505–510. [\[CrossRef\]](#)
- Rossi, S.; Calovi, M.; Velez, D.; Munoz, J. Munoz, Influence of addition of hard particles on the mechanical and chemical behavior of vitreous enamel. *Surf. Coat. Technol.* **2019**, *357*, 69–77. [\[CrossRef\]](#)

23. Benford, A.L.; Gorecki, A.; Gazo, L.J.; Baldwin, C.A. Enamel and Ground Coat Compositions. U.S. Patent 8,962,162, 15 July 2014.
24. Espargilliere, S.; Schanne, A.; Roques, F. Enamel Composition. CA Patents 2,409,576, 28 February 2006.
25. Aronica, A.; Coutouly, D.; Macaya, D.; Caisse, R. Hybrid Coating Compositions. CA Patents 2,409,567, 11 September 2001.
26. Haynes, W.M. *Handbook of Chemistry and Physics*, 92nd ed.; CRC Press: Boca Raton, FL, USA, 2011.

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