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Soil-resistant surfaces for traditional ceramics

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Abstract

Increasing demands for better cleanability have led to development of functional coatings on traditional glaze surfaces. However, mechanical and chemical durability of these coatings are not yet fully understood. In this work a traditional white sanitaryware glaze was coated with both commercial fluoropolymers and new hybrid sol–gel functional coatings. Also the influence of a transparent double-glaze on the surface properties was tested. Surface energy, hydrophobic and oleophobic properties of the surfaces were determined by contact angle measurements. Mechanical properties were evaluated by applying the accelerated abrasion tests by means of Erichsen apparatus. Chemical durability was determined in acidic, neutral and basic solutions. Cleanability of the surfaces was studied by FTIR technique with oleic acid as soiling agent. Surface topology and surface analysis were determined by scanning electron microscope and confocal optical microscope. The improved anti-soiling property of the coatings was due to the increased hydrophobicity and oleophobicity. The mechanical durability of the sol–gel coatings was shown to be highly dependent on the increased number of ceramic components. The coatings have good chemical durability in acidic and neutral environments but rapidly fail in alkaline solutions.

Keywords: Traditional ceramics; Surfaces; Mechanical properties; Functional applications; Coating

1. Introduction

Glazes are mostly used in everyday environments where it is important to enhance the soil and deposit repelling properties of the surface. Accordingly glazes are regarded as easy-to-clean surfaces. However, surface pitting and degradation in service diminishes cleanability.[1] Surface degradation might also lead to opening of closed porosity in the glaze thus leading to micro-scale holes which are often hard to clean by conventional cleaning techniques. In general, glazes have a good chemical durability in everyday environments. However, the durability is rapidly degraded in solutions of high or low pH. In acidic and neutral environments a hydrated surface film is formed as a result of ion exchange reaction between alkalis from the glass and hydrogen from the solution, while in basic environments the whole glass structure is attacked.

The interaction of the glasses with soiling components depends on both the surface topography and phase composition. The formation of deposits due to hardness of water, e.g. lime, magnesia and dissolved silicate species, also depends on the surface nano- and microstructure. Deposited spots containing lime and magnesia are effectively cleaned with acidic cleaning agents. However, the silicates in the spots bond chemically to the hydrated silicate layer, and consequently they are very hard to remove.[2] The deposited layer is likely to act as a site for soil and bacterial attachment. For increasing demands for e.g. hospital hygiene it is of utmost importance to develop surfaces, which have, besides desired surface appearance and mechanical properties also good chemical durability and minimum interaction with soiling components or different bacteria and biofilms.

The topography has a certain influence on the soil resistance and cleanability of the surface. On the other hand a well-controlled nanoscaled roughness of the surface increases the contact angle of liquids on the surface and thereby makes the surface soil-repelling. On the other hand increased smoothness of the surface has certain benefits for mechanical cleaning processes. Zircon silicate as opacifier in white, opaque glaze

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is known to affect the surface roughness of traditional glazes. Some of the zircon silicate crystals penetrate the upmost glassy surface layer thus increasing the roughness on micro-scale level. The smoothness aspect has been exploited in double glazed tiles where a second transparent layer has been applied on the standard white glaze in order to keep the white, opaque appearance of the glaze but with the enhanced cleanability of a smoother surface. Surface roughness will also be decreased by minimizing pinholes in the glaze surface.

Glazed surfaces have recently been coated with special functional layers to achieve soil-repelling surfaces. Commercial applications for sanitaryware and tiles are already available using hydro- and oleophobic coatings to enhance the water and oil repellence of the surface. Also self-cleaning surfaces based on the photo-catalytic activity of TiO_2 are available. Mechanical properties and chemical durability of new soil-repelling surfaces in service is still poorly understood.

The anti-soiling and easy-to-clean properties of surfaces can be improved by sol–gel hybrid coatings. Sol–gel hybrid coatings are promising new materials consisting of organic–inorganic composites with an amorphous nanoscale structure. The sol–gel coatings with thickness of about only a few hundreds nanometres to several micrometers consists of different parent substances that will build a nanoscale network through hydrolysis and condensation reactions. By using different precursors and process parameters the coatings have various combinations of properties depending on the structure and chemical nature of the coating[3]. The composition of the sol–gel coatings has a significant effect on the properties. Ceramic components give hardness while polymer components render the flexibility and repelling properties for tough and durable coatings.[4,5] By tailoring and optimising the composition of the sol–gel structure, the properties of the thin coating can be adjusted to desired directions. The hybrid thin coatings can be tailored for a good adhesion to many substrate materials. One of the major advantages of these coatings is their transparency to visible light and thereby, negligible changes in the appearance of the substrate.[6] Surface topography can also be modified by sol–gel coatings.

Fluoropolymer coatings have been commercially used for many years because of the surface properties of the fluorine atom. Fluor-based compounds generate surfaces with extremely low surface energies thus making the surfaces repellent to water and oil compounds.

In this work the influence of novel soil-resistant coatings and special double-glazed approaches for better soil-resistant of glazes are compared. Also, the mechanical and chemical durability of the coatings are measured.

2. Experimental

A standard white opaque sanitaryware glaze was used in this study. The glaze consists of typical raw materials with zircon silicate as opacifier. The glazes were prepared by milling the raw materials after which they were sprayed on tiles. The tiles were fired in an industrial gas kiln for sanitaryware. The firing cycle was 13 h and the peak temperature was 1235 °C.

Two silane-based experimental sol–gel coatings (PRO A and PRO B) and two commercial fluoropolymer coatings, F1 (ECC-1000 by 3M) and F2 (ECC-4000 by 3M), where applied on the glaze by spill coating and spraying. Before the coating process the glazes were cleaned with ethanol. The main composition of the sol–gel coatings varied in relation to the substances and the ratio between the polymeric and ceramic components. Ethanol was used as a solvent in the sol and water was added for the hydrolysis reaction. The fluoropolymer coatings were prepared by adding 0.1% of the commercial fluoropolymer to a slightly acidic ethanol solution. After coating most samples were heat-treated at 100 °C to form thin solid coatings through condensation reactions. The coating F2 was designed to be used without heat treatment thus only spraying of the solution on the sample was performed.

The smooth double-glazed sample (Transp) was prepared by glazing the once-fired white, opaque glaze with a transparent frit glaze. The frit had the same maturing temperature as the standard glaze. The tile was then fired a second time in an industrial gas kiln with a firing cycle of 18 h and a peak temperature of 1210 °C.

The data for the evaluation of wetting properties, surface free energy, hydrophobicity and oleophobocity of the non-coated and coated glaze samples were assessed with contact angle measurement (CAM 200 Optical Contact Angle Meter, KSV Instruments Ltd., CAM 200 software). The surface free energy measurements were carried out by using a solvent sequence containing distilled water and analytical grades of formamide, ethylene glycol and di-iodomethane. The contact angles of the probe liquids were used for calculations of the surface free energies of the substrates.[7] The assessments of hydrophobicity and oleophobicity of the non-coated and coated glaze surfaces were carried out by measuring the contact angle of distilled water and oleic acid ($C_{18}H_{34}O_2$).

The anti-soiling properties of the non-coated and coated glazed samples were assessed with soil-drop test developed at VTT. Each sample surface was contaminated with a spot of 0.5 um of oleic acid as soiling agent. The follow-up of the shape and spreading tendency of the oleic acid spot on the non-coated and coated test material surfaces was performed visually. Prior to the cleaning test, the oleic acid spot was dispersed on the sample surface with rubber teat with the load of 62 kPa. The contaminated sample surface was wiped with dry micro-fibre cloth with the load of 0.7 kPa approximately. The extent of oleic acid on the sample surfaces before and after cleaning was qualitatively assessed with FTIR mapping method (BioRad FTS 6000, Shadow Pro Mapping Software). The FTIR analyses carried out are based on the reflection technique with the exploitation of microscope facility. The IR ray is directed to the sample through the object lenses, which enables the adjusting of the measurable area with the exactness of 5 μm. The collection of IR spectra is carried out with motorised sample board and automating software. From the sample area of 150 μm × 150 μm, 196 IR spectra were collected and the collection was imaged as intensity difference map of stretching vibration between carbon and hydrogen atoms.

The wet abrasion resistance simulating the normal cleaning process of thin-coated ceramic glazes was measured with a wet abrasion test (modified standard DIN 53 778) by using the Erichsen washing apparatus designed for paint films. One sample of each coating type was exposed to 700 back and forth abrasion cycles and the respective replica samples were subjected to 1400 abrasion cycles. The abrasion was carried out with wetted (200%) micro-fibre cloth. The load applied on the sample was 0.7 kPa. The extent of the abrasion of the coated surfaces was assessed with contact angle measurements with water and oleic acid. The change in the specular-gloss of the coated surface was analysed with Micro-Tri-Gloss meter at 60° geometry.

Phase composition and surface structures of both non-coated and coated glazes was analysed with SEM/EDXA (LEO 1530 with a Vantage EFXA analyzer from Thermo Noram). Surface topography was measured by Confocal Optical Microscope, COM (μSurf by NanoFocus). Average surface roughness R_a, was measured for 250 μm × 250 μm surfaces, and surface roughness profile was measured for 1460 μm lines along the surface.

The chemical resistance of the coatings was obtained by measuring the contact angle after exposure to solutions with different pH values.

3. Results

The coatings selected to this study had all an adequate adhesion to the glazed ceramic substrate. Indications of brittleness or flaking off from the surface could not be visually observed.

The surface properties of the non-coated and coated glazed samples were studied by determining the surface energy values (Table 1). The effect of coatings on the hydrophobic and oleophobic properties was assessed by contact angle measurements of water and oleic acid on the surface as a function of time (Fig. 1). The surface of the standard glaze is rather hydrophilic in nature, the contact angle of distilled water is less than 30° and the total surface energy is about 60 mJ m^{-2}. Also the resistance against oil and greasy contaminants is weak as is shown by the contact angle measurements with oleic acid. The double-glazed (Transp) sample showed higher both hydro- and oleophobic properties. This is likely due to the decreased surface roughness. The surface energies show that the surface properties depend on the chemical composition of the coating. In general, coatings containing high concentrations of functionally modified polymers are hydrophobic. Increase of ceramic

Table 1
Surface energy values of the experimental surfaces with and without wet abrasion

Coating	Surface free energy (mJ m^{-2})								
	No abrasion			700 r			1400 r		
	γ^p	γ^d	γ^s	γ^p	γ^d	γ^s	γ^p	γ^d	γ^s
Std glaze	44.4	15.30	59.7	31.1	28.9	60.0	34.7	28.7	63.4
PRO A	11.0	33.8	44.8	17.3	27.4	44.7	23.2	30.7	53.9
PRO B	3.2	15.0	18.2	18.2	18.2	29.4	20.3	22.4	42.7
F1	3.9	11.3	15.2	12.7	16.4	29.1	18.9	21.7	40.6
F2	2.9	9.5	12.4	7.5	7.2	14.7	4.8	11.0	15.8
Transp	14.9	20.6	35.5	45.0	17.4	62.4	n.a.	n.a.	n.a.

γ^p is the polar and γ^d is the dispersive component of the surface energy γ^s.

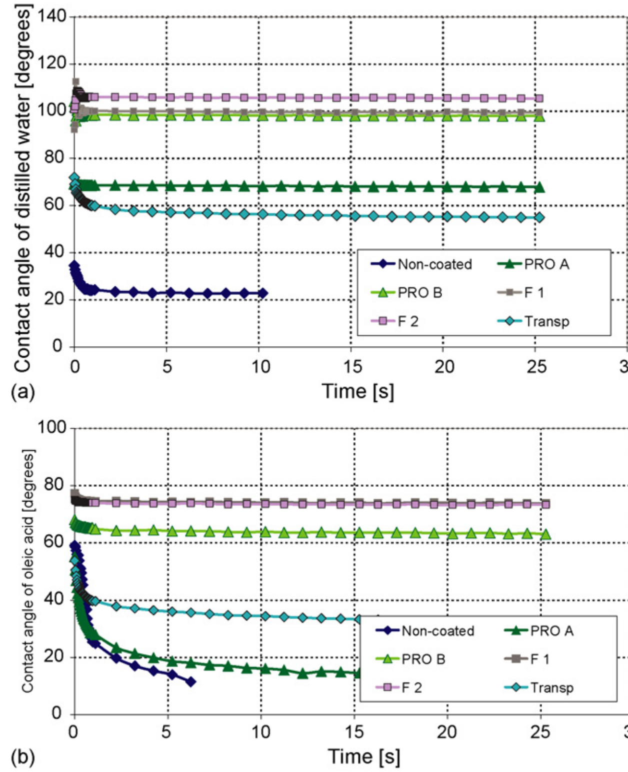

Fig. 1. Contact angles of distilled water (a) and oleic acid (b) on non-coated and coated glazed ceramic.

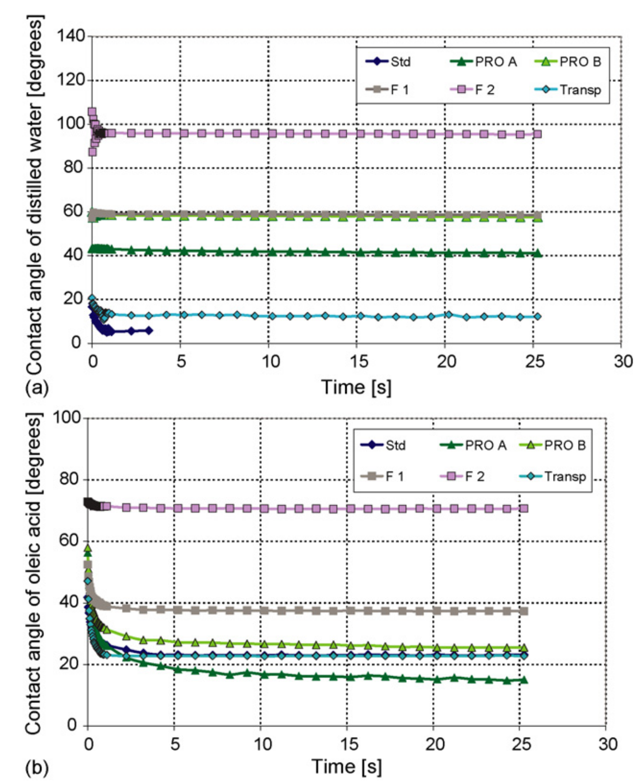

Fig. 2. Contact angles of distilled water (a) and oleic acid (b) on non-coated and coated glazed ceramic after 1400 abrasion cycles.

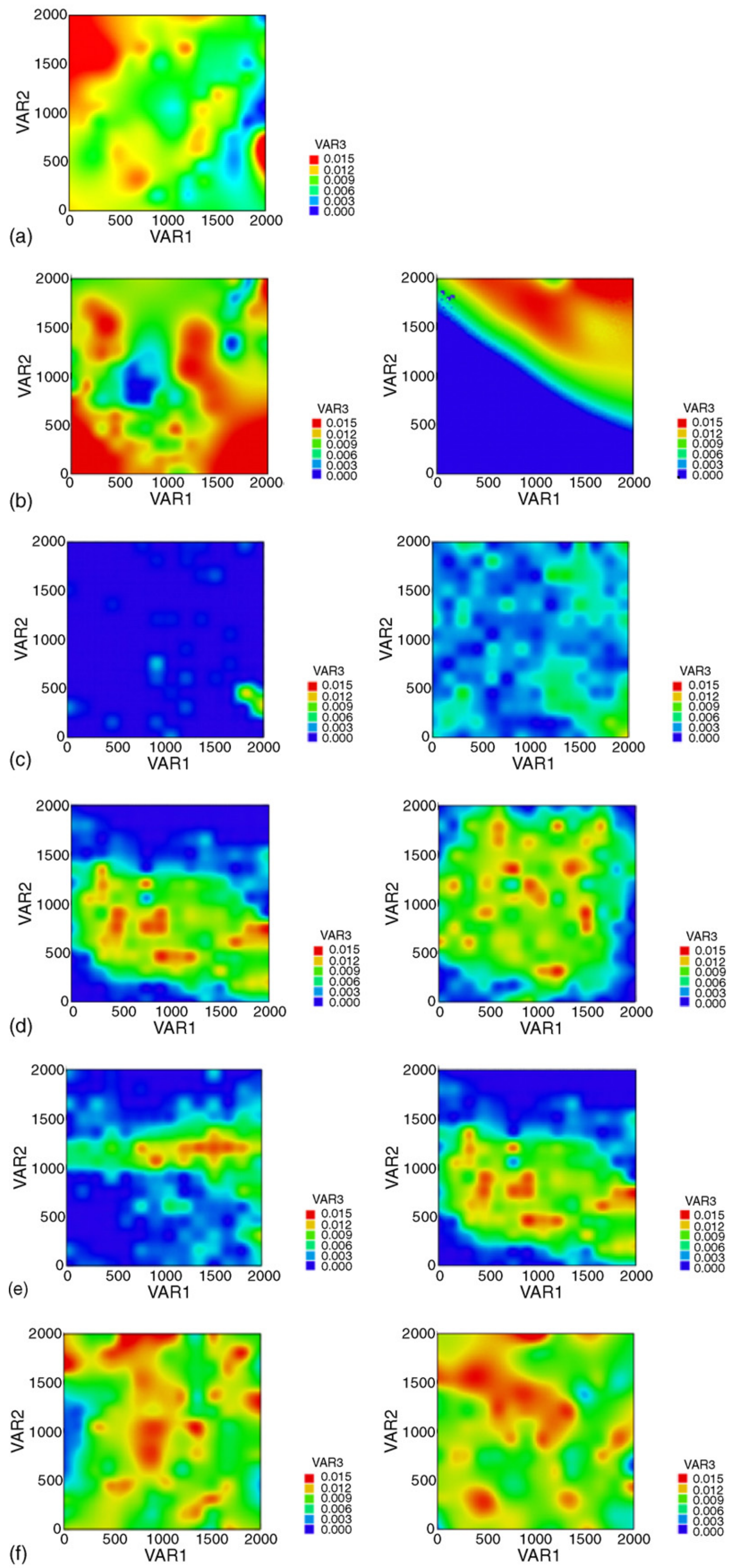

Fig. 3. FTIR charts showing oleic acid residues on non-coated and coated glaze surfaces after wiping the grease-covered surfaces with a dry microfibre cloth. The surfaces prior to the wet abrasion procedure are shown on the left side and the abraded surfaces on the right side. The light shades reveal that hydrocarbon-based soil is still present on the surface, while the dark (blue) areas are soil-free. (a) Std glaze, (b) PRO A, (c) PRO B, (d) F1, (e) F2, (f) Transp.

constituents in coatings may lead to decrease in hydrophobicity as suggested by Table 1, but was found to increase the durability against abrasion. Of the two novel experimental thin coatings PRO B with further modified polymeric content showed high hydrophobicity and oleophobicity. The more traditional ceramic nanocomposite coating, PRO A, increases the hydrophobicity of the surface but to a lower degree than the other coatings. The oleophobicity of PRO A was equal to the standard glaze. The commercial fluoropolymer coatings (F1 and F2) selected to this study are used as references to the novel experimental nanocomposite coatings. The hydrophobicity and oleophobicity of these commercial coatings are very good which is typical for coatings based on fluoropolymers.

Abrasion resistance of the coatings were evaluated from changes observed in the surface energy values when the coatings were subjected to the wet abrasion test (Table 1). Coatings with higher content of organic components in the matrix lead to softer surface structures, which are relatively susceptible to abrasion. The results indicate that the polymeric content of the coatings have a tendency to wear. The wearing can indirectly be estimated from the increase of dispersion and total surface energy values after abrasion and from the contact angle of water and oleic acid (Fig. 2). The surface energy values of the coating PRO A remained rather unchanged after 700 abrasion cycles, which is most likely due to the ceramic constituents in the coating. However, signs of wear also in this coating could be seen when the abrasion procedure was continued up to 1400 cycles. Surface properties of the coatings PRO B and F1 showed changes already after 700 abrasion cycles. After doubling the abrasion cycles, the surface energy values of these coatings nearly increased to the values of the non-coated reference glaze. The other fluoropolymer coating F2 was the only one that did not show any significant changes in surface energy after abrasion. Any explanation to the excellent mechanical properties of this coating could not be deduced from the surface analysis done in this work. Detailed compositional information about this commercial product was not available.

The anti-soiling properties and cleanability of the surfaces were studied by soil-spot-test and FTIR analysis (Fig. 3). The uncoated standard glaze was susceptible to oily stains and impurity contamination. Oleic acid drops spread on the surface and formed contaminated areas. Wipe cleaning with dry micro-fibre cloth had no significant cleaning effect of the surface. The anti-soiling properties of the coating with high content of ceramic components, PRO A, was also poor. All other coatings selected to this study improved the anti-soiling properties of the glaze surface. Oleic acid formed solid spots on the surfaces without any indications of spreading or penetration. The best result was obtained with the organically modified coating PRO B. The FTIR analysis showed that only traces of the oleic acid impurities could be detected after the cleaning with dry micro-fibre cloth. The anti-soiling properties of the other three coatings were clearly better to the uncoated glaze although a significant amount of oleic acid remained on the surface after the cleaning. The anti-soiling properties of the smooth, double-glazed tile was surprisingly equal to the standard glaze. Although the surface roughness was significantly lower ($R_a = 0.026$ μm), the soil-spot-test showed no improvement of the cleaning properties. The oily nature of the contaminant makes it probably sensitive to the oleophobic properties of the surface thus giving no differences in this test.

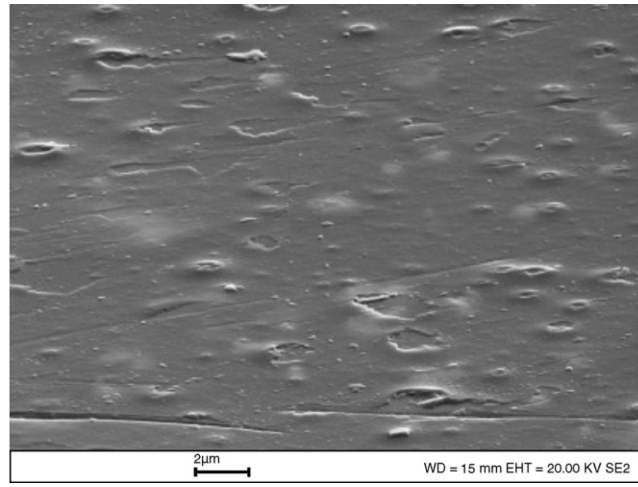

Fig. 4. SEM image of white opaque glaze coated with fluoropolymer F1 exposed to 700 abrasion cycles (×5000, 70° tilted).

The anti-soiling properties of all coatings after 700 abrasion cycles were decreased as shown by the soil-spot-test and FTIR analysis (Fig. 3). The SEM analysis showed that the coatings were damaged by the abrasion test (Fig. 4). The coating was partly peeled off thus revealing the uncoated glaze surface. Oleic acid was found to remain on the uncoated glaze after the cleaning process. The coated areas have a high oleophobicity and thus good resistance to the greasy oleic acid.

No changes in the surface roughness of coated samples compared to the standard glaze ($R_a = 0.059$ μm) could be observed, thus indicating that the coating is very thin. The only exception is the coating PRO B, which was found to give a smoother surface ($R_a = 0.039$ μm). The SEM analysis showed that the coating PRO B covered the whole glaze surface including the zircon silicate (Fig. 5). For the other coatings some of the zircon sil-

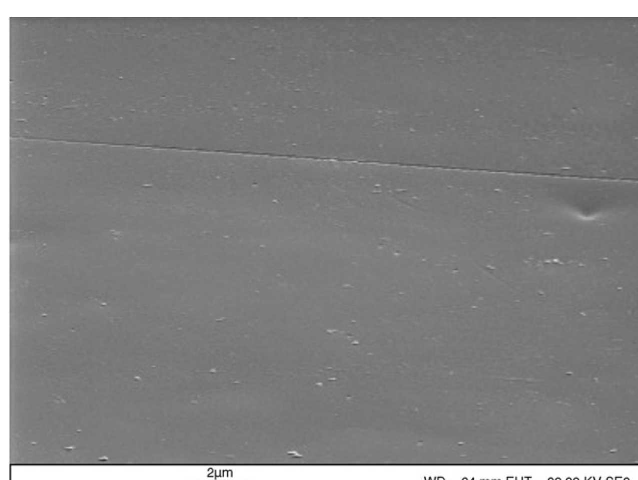

Fig. 5. SEM image of white opaque glaze coated with PRO B. The coating is covering all white zircon silicate crystals (×5000, 70° tilted).

icate crystals were still uncovered after the coating process. This explains the excellent results of PRO B in the soil-spot-test. After abrasion the surface roughness of PRO B increased ($R_a = 0.045\ \mu m$) thus also indicating a wear of the coating. PRO B led to a visible decrease in the gloss (80). PRO A showed a small decrease in gloss (85) but the glazes with the fluoropolymer coatings had unchanged gloss (90).

The chemical resistance of all coatings was good in acid and neutral solutions. No changes in hydrophobicity or visual appearance could be found. At pH > 10 a corrosion of the coatings could be noticed. After the attack the surface energy values were similar to the standard glaze. At pH 10 the coating was totally destroyed after 2 h and at pH 13 only 30 s was needed to destroy the coating. The poor chemical behavior of the coatings in alkaline solutions will put new demand on cleaning instructions for coated ceramics.

4. Conclusions

The anti-soiling properties of glazed surfaces can be improved by functional thin coatings. The chemical composition of the coating affects both its soil-repelling, chemical and mechanical properties. Sol–gel based coatings containing a high content of polymers increased the hydrophobicity and oleophobicity of the surface but decrease its abrasion resistance. The abrasion resistance can be improved up to a certain point by increasing the ceramic components in the coating matrix. Future challenge is to optimise the coating composition in a way that adequate abrasion resistance and satisfactory anti-soiling properties can be integrated within one coating. Coatings based on fluoropolymers effectively decrease the surface energy thus also the soiling of surfaces. Double-glazing with a transparent glaze decreases the surface roughness but has no effect on the attachment of oil based contaminants on the surface. All the coatings tested have a good chemical durability in acidic and neutral environments but are rapidly degraded in alkaline solutions. Although the coatings are not mechanically as durable as the uncoated glaze surface, they are potential alternatives when looking for novel surfaces for demanding environments with increased demands for e.g. hospital hygiene.

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