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The influence of the grain size distribution of raw materials on the selected surface properties of sanitary glazes

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Abstract

Glazes in significant way influence on most of the final properties of ceramic ware, mainly on surface parameters as colour, glossy or roughness. Usually, these properties has been changed by chemical composition and firing parameters. The results of presented works show, there is a possibility of improvement of surface proprieties by the selective milling and selection of the grain size of group of raw materials. It was shown, that in case of the sanitary glazes, an adequate selection of the grain size of quartz, feldspars, zirconium silicate and rest of raw materials, leads to improvement of whiteness and glossy as well as decreasing of roughness of surface.

Keywords: Glaze; Sanitary ware; Surface quality; Roughness; Whiteness; Glossy

1. Introduction

Ceramic glazes, forming thin glassy layer on ceramic products surface, play two basic roles: decorative and functional. Both are mutually combined and important from commercial point of view and they mainly depend on surface properties of the glazes [1–3,13,15]. Thus modifications of the surface properties play more and more important role in studies focused on ceramic glazes.

Several methods of surface quality improvement are used in ceramic technology. The most spectacular method is related to coating photo-catalytic TiO_2 film onto the glaze surface, followed by the glaze re-firing in the 850–900 °C temperature range [4]. Such formed coatings are hydrophobic, i.e. easily cleaned. Short life time of the TiO_2 layer resulting from low wear abrasive and scratch resistance is major disadvantage of this technology.

Another method consists in creating a double glaze layer onto the product [5–7]. The very thin films of transparent glaze milled to colloidal grain size was coated onto opaque or colored glaze [6]. During firing, this coating overflows, forming additional very smooth surface, improving its properties [5,7]. Particularly essential is defining the optimal parameters of such ceramic product firing: process duration [9] and time of the product exposition to maximal temperature [10]. Another method comprises of thin films coating, obtained by a sol–gel method, which contain organic and inorganic constituents of nano-metric grain size. These coatings are coated onto the fired product and then hardened in result of hydrolysis and condensation reactions occurring at temperature of about 100 °C. Exist also surfaces, where glazes are covered by polymeric coating by the usage of fluoric-polymer thin films [5,8].

Methods of surface properties modifications via limited changes of the glaze grain size, were also studied [11,12]. All these studies proved that glaze grain size reduction down to definite level results in gradual decrease of the molten glaze viscosity, what favors avoiding of gas bubble formation, better glossy and improved smoothness of the glazes. From the other side, fine glaze grains in raw state increase plasticity and shrinkage, what may result in cracking and crawling during firing process (Fig. 12). Very fine-grained suspensions are also characterized by a higher tension what increases air absorption during the glazing process and finally favors the formation of bubbles within the coated glaze. The present study is aimed at glaze surface properties modification, obtained in result of selective milling of the raw materials down to the sub-micron fractions.

2. Materials and methods

Three types of new glazes having mole composition shown in Table 1, were used in experiments. For comparison, a

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Table 1
Mole composition of experimental glazes.

Glaze oxides	Glazes series			
	2.xx	3.xx	4.xx	
CaO + MgO	0.65	0.75	0.64	
$Na_2O + K_2O$	0.23	0.22	0.23	
ZnO	0.12	0.03	0.13	
SiO_2/Al_2O_3	9.78	10.07	9.75	
Zirconia	0.26	0.26	–	0.25[a]

[a] Glaze 4.07 and 4.08.

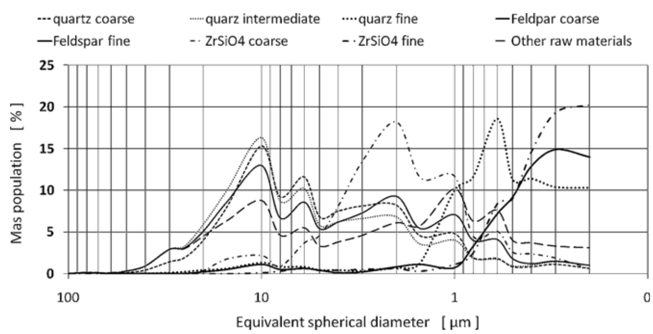

Fig. 1. Examples of grain size distribution of selected raw materials used for preparation of glazes compositions.

commercial glaze taken from a production line of a Polish factory producing sanitary products, was also used. The experimental glaze were composed of the commonly accessible standard raw materials. The samples were prepared in laboratory conditions. Separately, three raw material groups: quartz-based (quartz MK40P from SKSM Sobótka and AKV Sicron), feldspar-based (feldspars: *Forschammar*, *Norfloat Na600*, *Norfloat K600 and Norflux Nord Cape Minerals*) and the others (*Wollastonite O95 Ottavi*, *Talc Luzenac*, *Kaolinite KOC Surmin_Kaolin*, *ZnO*), were milled. In two cases, very fine-grained of zirconium silicate (Kreuzonite) were used as well. Examples of grain size distribution of chosen raw materials: quartz-based, feldspar-based, zirconium silicate-based and others, are shown in Fig. 1, whereas the rule of the glaze grain size selection via comparison of mean values d_{50} of individual groups, are shown in Tables 2–4. Final sets of glazes were obtained in result of intensive homogenization of components. Final glaze slurry had density of 1.74–1.75 g/cm^3 and fluidity corresponding to a outflow time from a 4 mm Ford Cup of equivalent to 125–130 s. Discs of 5 cm diameter of a sanitary mass Vitreous China were coated with glaze and then fired in laboratory kiln, heated up to 1230 °C for 4 h and hold at maximum temperature for 1 h. Measurements of whiteness and glossy were made using spectrometer Konica-Minolta CM-700d. Roughness (mechanical with use of profilometre Hommel Tester T500 and optical with use of confocal microscope Olympus Lext OLS4000), was also characterized. Additionally, observations of the glaze surface by confocal microscope OLS 4000, optical microscope Nikkon AZ100 and SEM Nova Nano SEM200, have been conducted. Results of glossy, whiteness and roughness determined for individual groups of glazes are shown in Tables 2–4 and in Figs. 2–4, whereas microscope images of the surface are shown in Figs. 5–10.

3. Results and discussion

The following criteria describing the glazes surface features were chosen in the present study: whiteness and glossy

Table 2
Average grain size composition of each group of component used for each experimental glaze of the 2.xx series and results of changes of colour and glossy differences from reference 2.00 glaze and roughness.

Glaze series	Glaze mark	Quartz	Feldspars	Others	Zircon silicate	Difference between reference 2.00 glaze and experimental glazes			Roughness
	Average grain size (d_{50}) of glaze components [μm]					Color difference ΔE_{00}		Glossy difference ΔG	R_a [nm]
Commercial glaze (d_{50} = 3.32 μm)									125
Series 2.xx	2.00	Milled together component (glaze d_{50} = 3.00 μm)							180
	2.09	8.33	0.5[a]/0.37[b]	2.68	1.37	1.78		4.26	130
	2.01	1.44				1.78		3.17	150
	2.03	0.37				0.58		1.18	130
	2.12	0.27				1.74		4.65	120
	2.18	8.33	0.15[c]	2.68	1.37	1.29		2.05	170
	2.19	0.27				1.90		3.22	160
	2.10	0.37	4.07[a]/5.22[b]	2.68	1.37	1.78		3.61	100
	2.03		0.5[a]/0.37[b]			0.58		1.18	130
	2.11		0.25[a]/0.24[b]			1.74		4.25	130
	2.03	0.37	0.5[a]/0.37[b]	2.68	1.37	0.58	–	1.18	130
	2.13				0.25	2.28	2.15[d]	8.68	140
	2.13	0.37	0.5[a]/0.37[b]	2.68	0.25	2.28		4.01	140
	2.14			0.51		1.85		5.72	70

[a] Feldsparr Forschammar.
[b] Feldspar Norflux.
[c] Milled together.
[d] Differences ΔE_{00} calculated relative to glaze 2.03.

Table 3
Average grain size composition of each group of component used for each experimental glaze of the 3.xx series and results of changes of colour and glossy difference from reference 3.00 glaze and roughness.

Glaze series	Glaze mark	Quartz	Feldspars	Others	Zircon silicate	Difference between reference 3.00 glaze and experimental glazes		Roughness
		Average grain size (d_{50}) of glaze components [μm]				Color difference	Brightness difference	
						ΔE_{00}	ΔG	R_a [nm]
Series 3.xx	3.00	Milled together (glaze d_{50} = 3.48 μm)				–	–	110
	3.10	2.02	0.44/0.37	3.99	1.37	0.65	2.20	110
	3.01	1.23				0.62	2.16	100
	3.03	0.19				0.87	2.91	150
	3.12	1.23	0.11	3.99	1.37	0.86	2.77	90
	3.11	0.19				1.29	4.57	90
	3.09	2.02	4.59[a]/4.58[b]	3.99	1.37	1.00	3.49	60
	3.01		0.44[a]/0.37[b]			0.62	2.16	100
	3.01	2.02	0.44[a]/0.37[b]	3.99	1.37	0.62	2.16	100
	3.02		0.44[a]/0.18[b]			1.31	4.61	90

[a] Feldspar Na-600.
[b] Feldspar K-600.

Table 4
Average grain size composition of each group of component used for each experimental glaze of the 4.xx series and results of changes of colour and glossy difference from reference 4.00 glaze and roughness.

Glaze series	Glaze mark	Quartz	Feldspars	Others	Zircon silicate	Difference between reference 4.00 glaze and experimental glazes		Roughness
		Average grain size (d_{50}) of glaze components [μm]				Color difference ΔE_{00}	Brightness difference ΔB	R_a [nm]
Series 4.xx	4.00	Milled together (glaze d_{50} = 1.98 μm)				–	–	50
	4.01	6.67	5.82	2.72	–		−0.24	84
	4.02	0.57					−0.34	55
	4.04	0.36					0.58	53
	4.06	6.67	0.34	2.72	–		1.44	54
	4.03	0.57					−3.34	36
	4.05	0.36					−3.45	28
	4.01	6.67	5.82	2.72	–		−0.24	84
	4.06		0.34				1.44	54
	4.04	0.36	5.82	2.72	–		0.58	53
	4.05		0.34				−3.45	28
	4.07	0.36	0.34	2.72	2.04	–	–	56
	4.08				0.34	2.92[a]	10.19[a]	118

[a] Differences ΔE_{00} ΔB calculated relative to glaze 4.07.

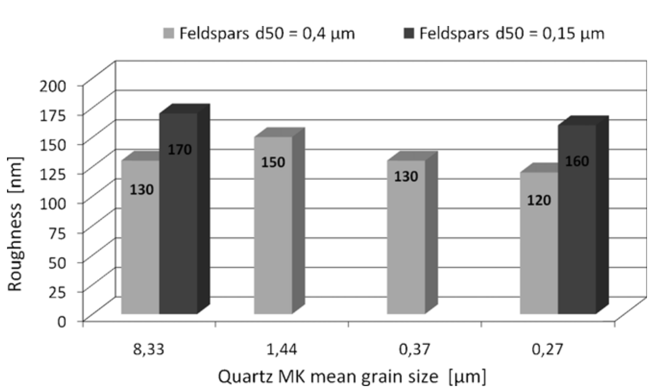

Fig. 2. Roughness R_a of some experimental glazes of the 2.xx series in function of Quartz MK d_{50} grain size (*for two different d_{50} Feldspars mixture grain sizes*).

differences and roughness [11,13,14]. This choice results from the assumption that these parameters are the most important for the tested sanitary glazes. The reference for each series is a glaze of the same molar composition but prepared in traditional manner, with a grain size similar to production glaze. In case of the roughness, for comparative purposes, reference glazes were fired together with experimental glazes in laboratory kiln.

Glossy changes were determined by calculation of a glossy difference ΔG between experimental glaze and reference glaze, marked in each case with a symbol X.00, where x is a series number. Positive value indicates improvement of the glaze glossy.

Similarly, for whiteness its difference, was determined from the reference glaze. The model CIEDE 2000 [16], ΔE_{00}, established in 2001 especially for small colour differences, was

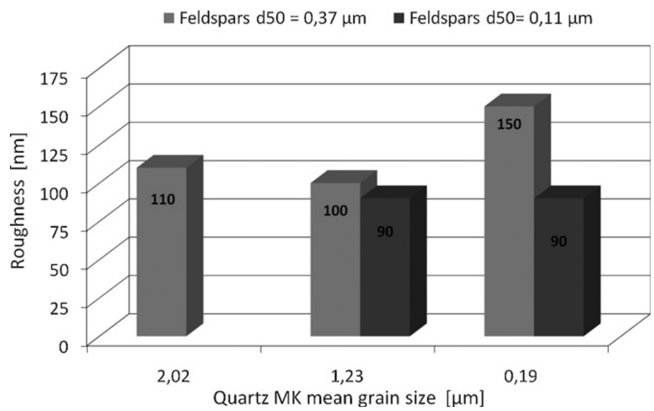

Fig. 3. Roughness R_a of some experimental glazes of the 3.xx series in function of Quartz MK d_{50} grain size (*for two different d_{50} Feldspars mixture grain sizes*).

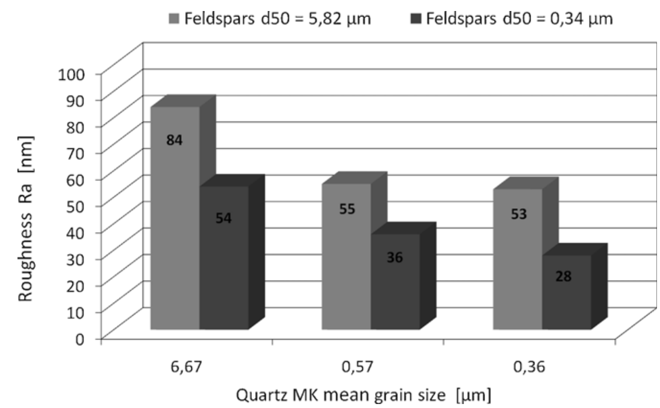

Fig. 4. Roughness R_a of some experimental glazes of the 4.xx series in function of Quartz MK d_{50} grain size (*for two different d_{50} Feldspars mixture grain sizes*).

used for calculations of the whiteness tonality. The CIDE 2000 formula is based on CIELAB colour space and allows to calculate the colour difference ΔE_{00} between two samples with pair of colour values, L_1, a_1, b_1 and L_2, a_2, b_2.

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_\tau \frac{\Delta C'}{S_c} + \frac{\Delta H'}{S_H}}$$

where $\Delta L'$ – lightness difference; $\Delta C'$ – chroma difference; $\Delta H'$ – hue difference; k_L, k_C, k_H – lightness, chroma and hue weighting factors; S_L – lightness weighting function; S_C – chroma weighting function; S_H – hue weighting function; R_τ – a function (the so-called rotation term) that accounts for the interaction between chroma and hue differences in the blue region.

On the colour difference scale a ΔE_{00} ranged between 0 and 1 corresponds to an invisible colour difference, between 1 and 2 the difference is visible only by experienced observer, and over 2 the colour difference is seen by each observer.

The new method of preparation of glazess based on well defined grain size of groups of raw materials. Raw materials

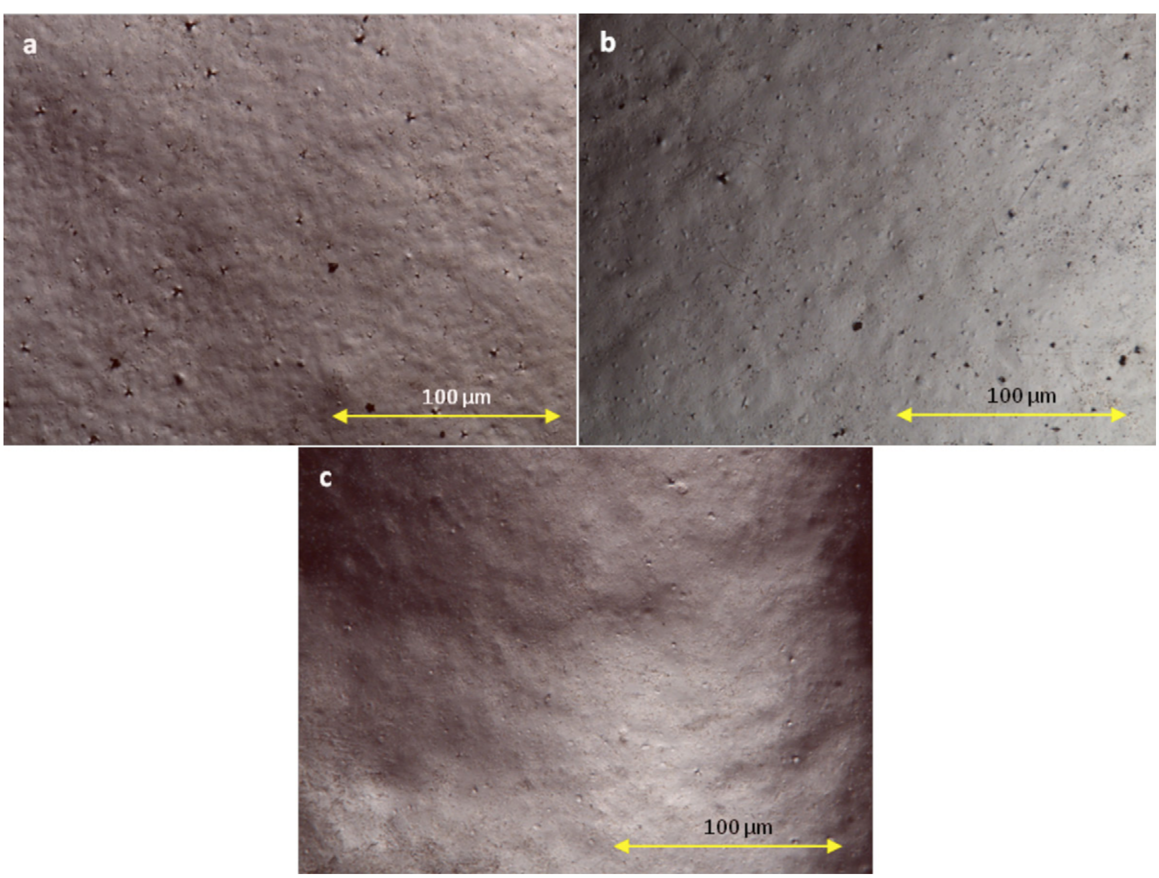

Fig. 5. Images of glazes surface of (a) 2.00; (b) 2.18; (c) 2.19 sample (variable – grain size of quartz, constant – grain size of other raw materials – Table 2).

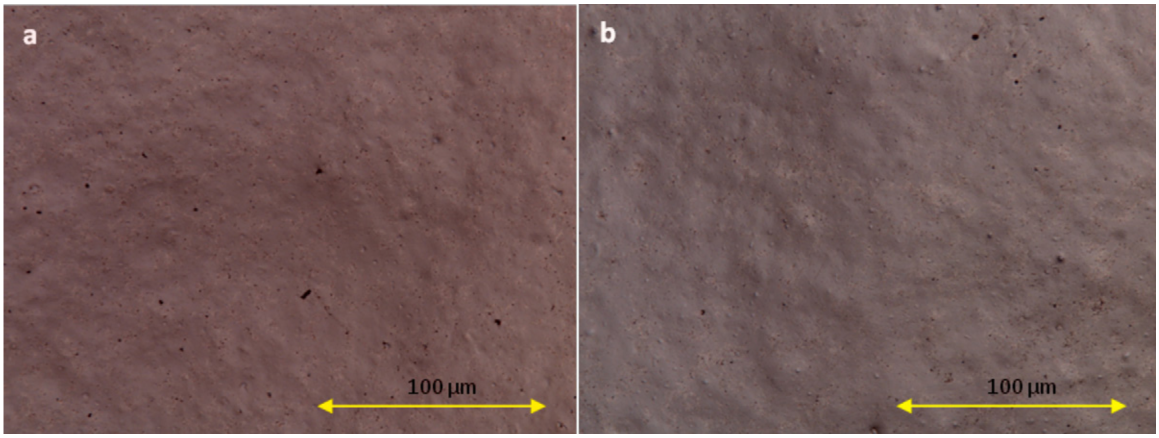

Fig. 6. Images of glazes surface of (a) 2.10; (b) 1.11 sample (variable – grain size of feldspars, constant – grain size of other raw materials – Table 2).

were divided into four groups: Quartz, Feldspars, Zircon silicate and all the others (wollastonite, talc, kaoline and zinc oxide). They were separately milled in order to obtain each specified grain size. The composition of each glaze, was chosen in order to the grain size of three groups of raw materials constant and change only one (Tables 2–4). For example in glazes marked as 2.09; 2.01; 2.03; 2.12 (Table 2) they have a constant grain size of feldspar, $ZrSiO_4$ and all others and the only difference is in grain size of quartz. Than it is possible to study how the change of grains size of one kind of raw materials affects parameters like whiteness, glossy differences and roughness.

Experimental glazes from series 2.xx and 3.xx are white. Glaze from series 4.xx, are transparent (4.01–4.05) and those with numbers 4.07 and 4.08 are white (after introduction of various grain sizes of zirconium silicate). Calculations of white colour differences were thus conducted for all glazes from series 2.xx and 3.xx, as well as between glazes 4.07 and 4.08. Glossy

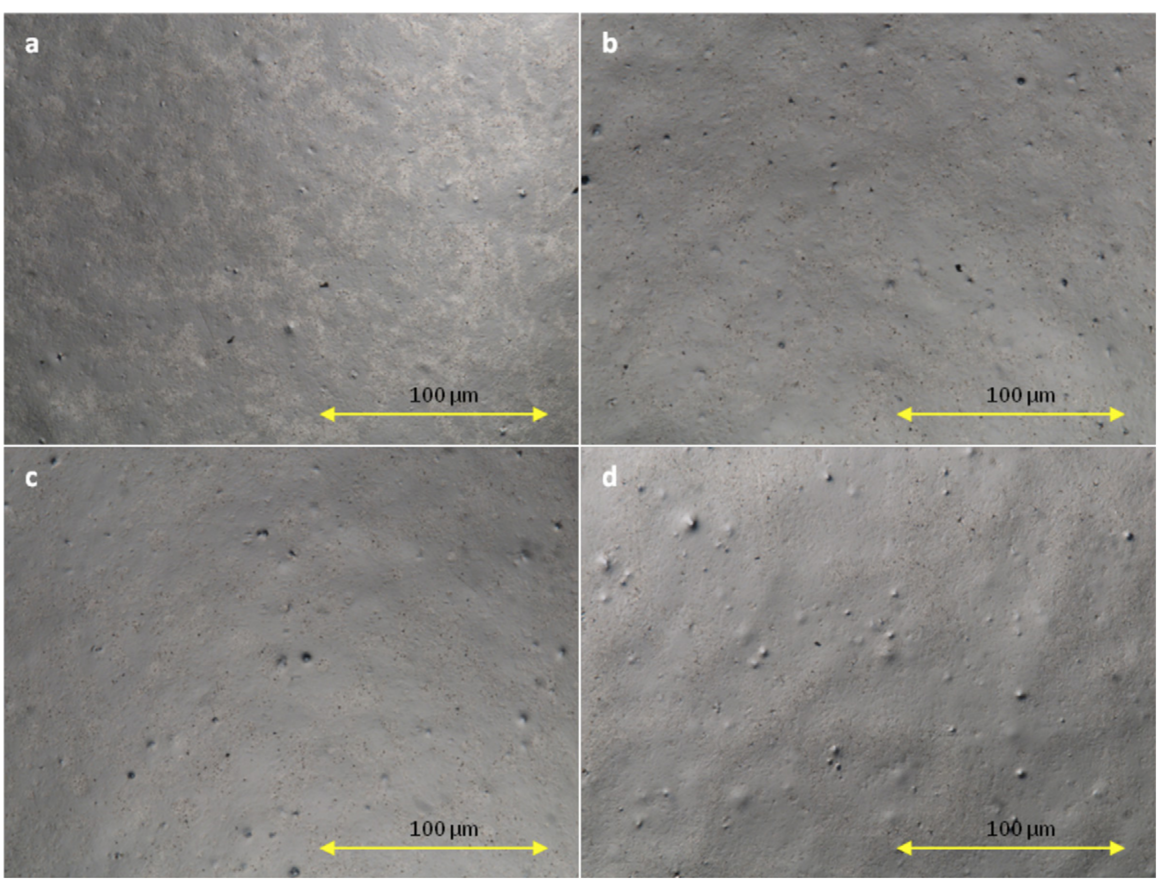

Fig. 7. Images of glazes surface of (a) 3.00; (b) 3.10; (c) 3.01; (d) 3.03 sample (variable – grain size of quartz, constant – 0 grain size of other raw materials – Table 3).

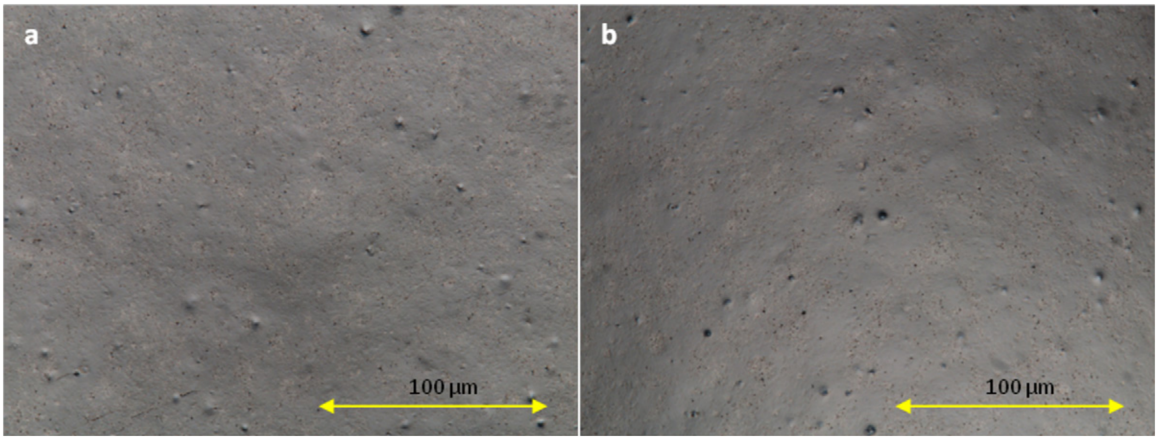

Fig. 8. Images of glazes surface of (a) 3.09; (b) 3.01 sample (variable – grain size of feldspars, constant – grain size of other raw materials – Table 3).

differences were calculated for all glazes of the series: 2.xx; 3.xx and 4.xx. Results obtained for white glazes of the series 2.xx and 3.xx (Tables 2 and 3 and Figs. 2, 3, 5–8), proved their similar behavior. Using constant medium grain size of feldspar and decreasing grain size of quartz achieved visible improvement of gloss and no changes in whiteness. Using very fine grain size of feldspars and reduced quartz grain size lead to visible glossy and whiteness improvements, without roughness change.

However, it results from analysis of transparent glazes (4.01–4.05) that finding relation between glossy and grain size changes of individual groups of the raw materials is not possible. This can be explained by a unequal transparency, resulting from the differences of the glaze fusibility and viscosity, or can be related with glaze thickness difference. It can also result from different refractivity indexes due to glaze density difference after firing. Otherwise, essential influence of the grain size onto roughness was observed for tested glazes. Reduction of the grain size of each group of the raw materials, results in an improvement of the glaze surface. For the best glaze (4.05), in which feldspar fine grains ($d_{50} = 0.34$ µm) and

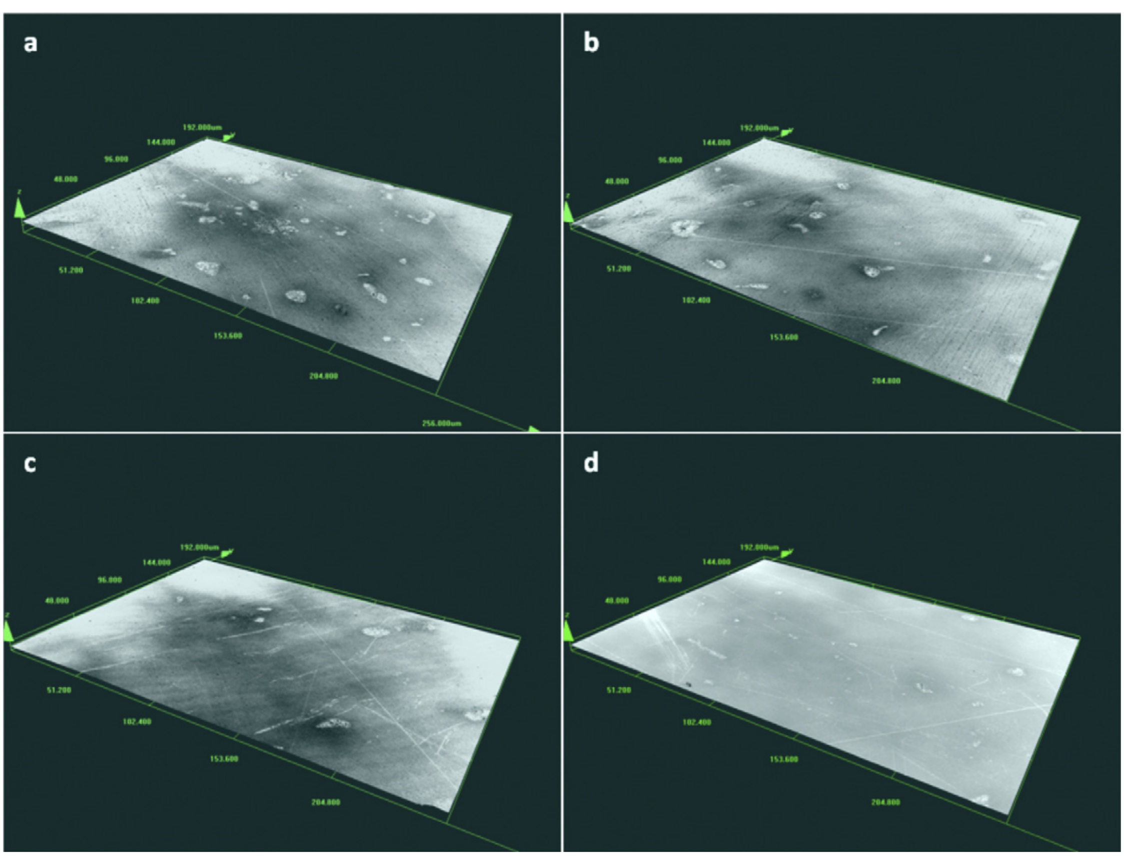

Fig. 9. Images of glazes surface of (a) 4.00; (b) 4.01; (c) 4.02; (d) 4.04 sample (variable – grain size of quartz, constant – grain size of other raw materials – Table 4).

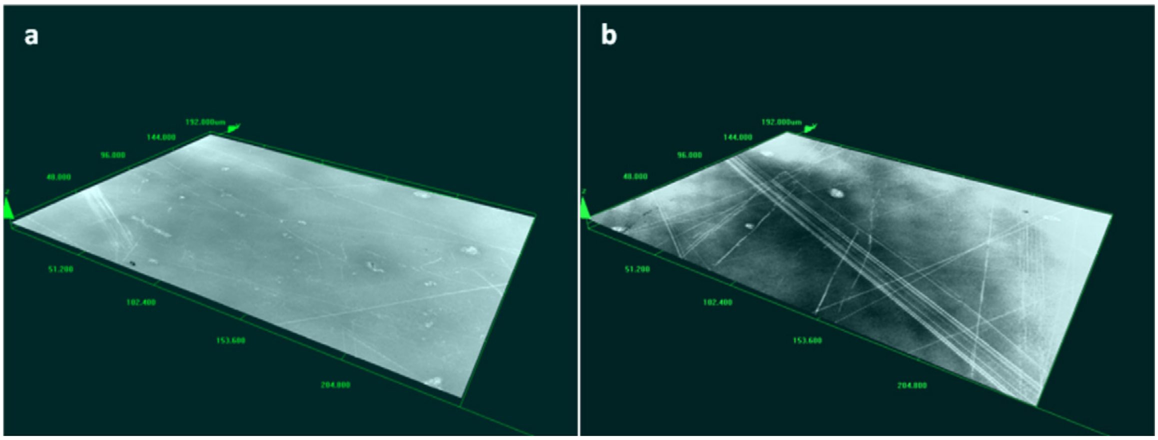

Fig. 10. Images of glazes surface of (a) 4.04; (b) 4.05 sample (variable – grain size of feldspars, constant – grain size of other raw materials – Table 4).

quartz fine grains (d_{50} = 0.36 μm) were used, a roughness of 28 nm was obtained. In most cases, the roughness values range from 50 to over 80 nm.

Addition of $ZrSiO_4$ of the coarse and fine grain size (glazes: 2.03; 2.13 and 4.07; 4.08), indicates that in sanitary glazes, zircon silicate (Table 4) is responsible for the roughness. Introduction of the zircon silicate of the grain size 2.04 μm, rises up mean value of the roughness R_a from value 28–56 nm, and introduction of zirconium silicate with d_{50} = 0.34 μm, results in raise of R_a up to 118 nm. Similar effect, but at a smaller scale, is observed for the 2.xx series (glazes 2.03 and 2.13), where the reduction of the zirconium silicate grain size results in a roughness increase of about 7% (Table 2). It can be explained by the $ZrSiO_4$ grain size distribution inside the final glazes 2.03 and 2.13 (see Fig. 11). The zirconium silicate grains tend to concentrate, what causes areas with different $ZrSiO_4$ concentrations and in these areas some grains can protrude over the glaze surface. Application of finer-grained $ZrSiO_4$, more numerous grains per volume unit, results in the worse surface smoothness. An improvement of homogenization of $ZrSiO_4$ in glazes, should solve this problem. Otherwise, reduction of zirconium silicate grains size in the 2.xx and 4.xx series, has advantageous influence onto the glaze whiteness and glossy. By comparison of differences between the reference and experimental glazes (Tables 2–4) it was shown an improvement of smoothness, whiteness and glossy for glazes from the series 3.xx and 4.xx similar to glazes from series 2.xx.

An examination of the results reported in Tables 2–4 shows that careful selection of the grain size of each individual group of the raw materials can considerably improve the glaze surface properties. It can observed that in most of tested cases the phenomenon of glaze crawling, common in case of overmilling (Fig. 12), was not observed for the tested materials. Such a procedure of glaze preparation can be easily implemented, because attritor or agitator bead type mills, able to get very fine grains within narrow size distribution, are more and more often used.

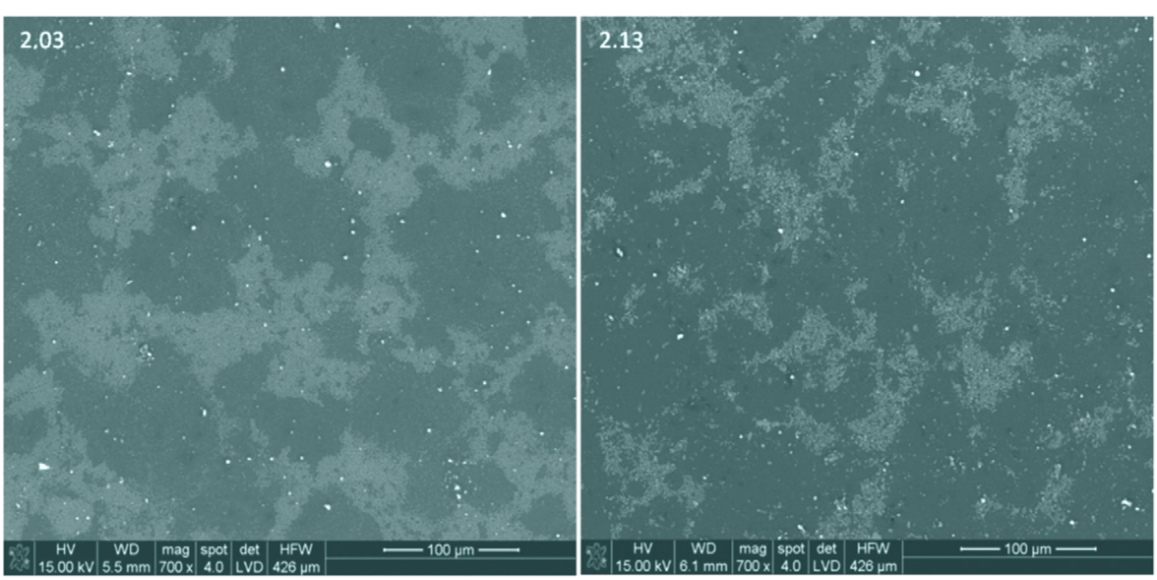

Fig. 11. SEM images of surface of glazes 2.03 and 2.13, prepared with different grain sizes of zircon silicate.

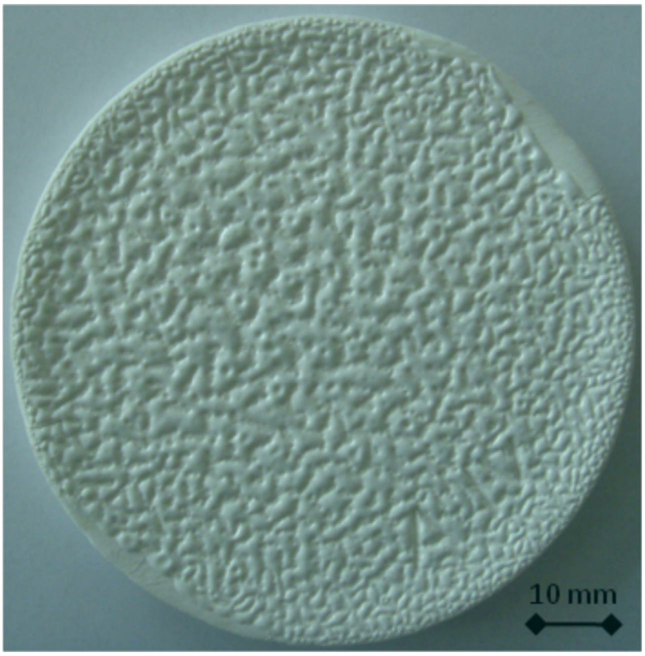

Fig. 12. Microscopy image of rolled glaze 2.00 when all components are milled altogether to submicronic grain size (d_{50} = 0.22 μm).

4. Conclusions

- The preparation of glazes by using controlled grain size raw materials can advantageously influence the surface properties of ceramic glazes (Tables 2–4).
- It was observed that the obtained changes of glaze surface are depending on the glaze composition (Tables 1–4).
- Decrease of the zirconium silicate grain size can considerably improve the glaze whiteness and glossy, with disadvantageous influence onto the roughness (sample: 2.03; 2.13; 4.07; 4.08).
- Independent optimization of quartz and feldspar grain size is suggested for obtaining the most advantageous glaze surface feature (sample: 2.14; 3.02; 3.11; 3.12; 4.05).

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