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# NON-TYPICAL DEFECTS ON SURFACES OF CERAMIC AND ROOF TILES: NATURE AND THE CAUSES

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***Abstract:*** This research was conducted to identify the nature and the cause of non-typical defects which appeared on the visible surfaces of ceramic and roof tiles. Microstructural analysis was conducted via optical microscope and scanning electron microscope coupled with energy dispersive spectrometer. Ceramic tiles contained black spots and dark brown clusters with yellow halos. Black spots originated from carbon contained in starting glaze raw materials. EDS analysis of clusters of dark-brown color in the pores showed the presence of Fe, which is found to affect the quality of the visible tile surface. Non-homogeneities on the roof tiles surfaces appeared in the form of stains and manifested after immersions in water or aspersing water on the tile surface. The cause of inhomogeneities was a local phenomenon due to the porous structure of micro cracks caused by coarse metallic grains that are imported with the raw materials.

***Key words:*** ceramic tiles; roof tiles; surface defects; impurities; microstructural analysis.

## 1. INTRODUCTION

The application of materials with high performances is widely spread in the contemporary architecture. When it comes to façade materials, besides quality, the visual appearance is highly estimated. Incessantly, facades of the buildings are made of ceramic tiles that also have a certain structural function, [1, 8, 9]. In the present study, a commercial edifice (in Aranđelovac, Serbia) was sheathed with ceramic tiles sizing 120×60 cm. The tiles were manufactured in Italy. Their characteristics corresponded to the valid standard according to the product declaration, and they were categorized as pressed ceramic glazed tiles of BIa type with low water absorption ($E \leq 0.5$ %), class 1, [10]. The investigated tiles were of class 4 according to surface abrasion. The tiles were classified as GA when (household) chemical resistance was tested, class GLA towards resistance to small quantities of acids and bases, and the class 5 according to resistance to stains, [10]. According to the Standard requirements, the ceramic tiles can be utilized for sheathing of the exterior floors and walls.

Clay roof tiles are categorized as traditional ceramic materials. Since clay roof tiles occupy an important place in modern architecture, they must correspond to a number of requirements concerning their quality and have adequate visual appearance. In this study, nature and causes of appearance of inhomogeneities on the roof tiles surfaces that deteriorated the exquisite visual characteristics were investigated.

## 2. EXPERIMENTAL WORK, ACHIEVED RESULTS AND DISCUSSION

### 2.1 Defects on visible surfaces of ceramic tiles

In order to determine the nature and the cause of the defects on the visible surface of the ceramic glazed tiles, two groups of tiles were sampled as follows: each group contained 10 tiles from every palette/package. The established marks were: 1. Tiles taken from the fabric palette (Sample 1); and 2. Tiles peeled from the facade (Sample 2). The following experiment was conducted for determination of possibility of defects formation on the visible surfaces of tiles during whetting of the product or after contact with iron structures. A beam of sparks originating from the whetting process was directed towards visible tile surface. The tile sample tested in described manner was marked as Sample 3. The following investigations were conducted:

1. Visual examination of the visible tile surfaces (visually);
2. Testing of the certain parts of tiles by using optical microscope;
3. Testing of the certain parts of tiles via SEM/EDS analysis in number of testing spots.

The quality of the tiles' surfaces was conducted by visual examination in accordance with the standard, [11] – Part 2. Parts of the tiles' surfaces were analyzed by an optical microscope LEICA MZ6. The samples prepared for optical microscopy testing were used in SEM-EDS analysis as well. Defects were analyzed by a scanning electron microscope (JEOL JSM-6610 LV), accompanied with detector for microanalysis. For the SEM analysis, the samples were coated with Au films to improve the conductivity prior to imaging.

The sample which was taken from the fabric palette (Sample 1) contained empty pores and pores filled with certain black substance in the visible superficial

layers, i.e. glaze. According to the requirements of the Standards (SRPS EN 14411:2012; SRPS EN ISO 10545-2:2012), the appearance of the pores does not influence the quality of visible surface. The superficial layers/glaze of the samples peeled from the façade (Sample 2) contained the pores surrounded with the yellow „halo“ and filled with dark brown substance, pores filled with dark brown substance, and pores filled with black substance, and also empty pores. According to the requirements of the Standards (SRPS EN 14411:2012; SRPS EN ISO 10545-2:2012) the appearance of the pores filled with brown substance and yellow halo deteriorate the quality of a visible surface and such tiles are considered defected.
The visible surface of the Sample 1 was examined via optical microscope. The surface is of white color, non-homogenous, husky/coarse and exhibiting pearly effulgence. The non-filled, round-shaped pores with mean diameter from 0.3 to 1 mm are present. Besides these voids, smaller irregularly shaped pores with mean diameter below 0.3 mm are also appearing. These pores contain black colored substance. Spots are occasionally present without presence of the voids. Fig. 1. presents an optical microscope microphotograph of the Sample 1 surface.

Fig. 1. Optical microphotograph of the Sample 1

The visible surface of the Sample 2 was also examined via optical microscope. The analyzed defects were as follows: round pores filled with dark brown substance and circled by a yellow halo, round pores filled with dark brown and black substance, empty voids or pores with black substance. In the Fig. 2, an optical microscope microphotograph of Sample 2 surface is given.
Defects on the surfaces of the tiles (Samples 1, 2 and 3) were recorded via SEM, and the EDS analysis in certain spots was conducted. In the Fig. 3 and 4, recordings of the Sample 1 performed on two different places/spots are given: a defect on the surface – an empty pore (Fig. 3.) and defect – pore with black substance (Fig. 4.).

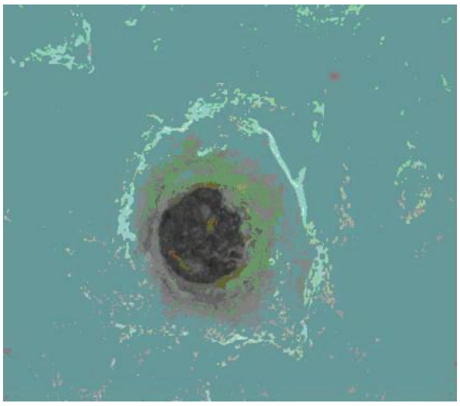

Fig. 2. Optical microphotograph of the Sample 2

In the Fig. 5 and 6 recordings of the Sample 2 performed in two different places/spots are given: a circular pore filled with dark brown substance with yellow halo (Fig. 5.) and pore filled with dark brown and black substance (Fig. 6.). In the Fig. 7 and 8, recordings of the Sample 3 are given: a defect on the surface in form of irregularly shaped dark brown pile (Fig. 7.) and cross section of the tile with the defect in the form of irregularly shaped dark brown pile (Fig. 8.). EDS analyses of the recorded defects were performed, and the investigated spots are given in the SEM recording (Spectrum 1, 2). Results of the EDS analysis are given in Table 1.

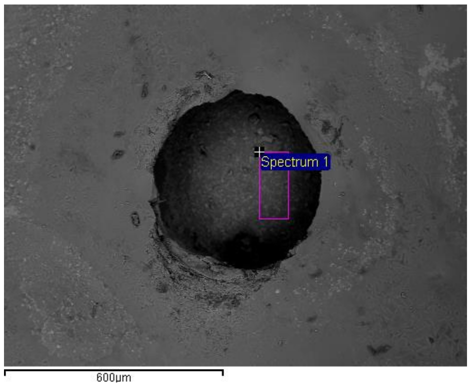


Fig. 3. SEM microphotograph of the Sample 1: empty pore

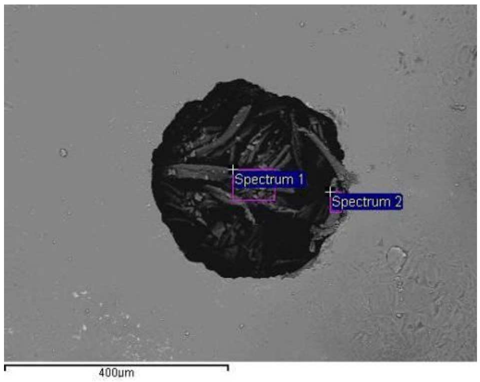


Fig. 4. SEM microphotograph of the Sample 1: pore with black substance

Defects that were present on the surface of the Sample 1 are of following types: empty pore or pore filled with black substance. A characteristic circular pore is recorded via SEM and illustrated in Fig. 3. Microanalysis on of the empty pore highlighted the presence of the elements characteristic for the ceramic materials (glaze), [3, 5, 6]. One characteristic round empty pore filled with black substance is recorded by SEM and given in Fig. 4. EDS microanalysis of the fiber shaped inclusion pointed out on the dominant presence of the carbon.

Table 1. Results of EDS analyzes of Samples 1, 2 and 3

| S. | Fig/Spot | Na | Mg | Al | Si | K | Ca |
|---|---|---|---|---|---|---|---|
| 1 | 3/ 1 | 3.73 | 2.35 | 8.99 | 24.24 | 1.55 | 405 |
| 1 | 4/1 | 0.60 | | 1.21 | 3.61 | 0.29 | 123 |
| 1 | 4/ 2 | 0.29 | | 0.40 | 1.29 | | 0,29 |
| 2 | 5/1 | | | 0.60 | 1.97 | | 082 |
| 2 | 6/1 | | 1.18 | 1.83 | 3.80 | | 105 |
| 2 | 6/2 | 0.21 | | 0.52 | 1.57 | | 0.22 |
| 3 | 7/1 | | 0.88 | 0.93 | 2.98 | | 0.94 |
| 3 | 7/2 | | 0.27 | 0.48 | 1.68 | | 0.71 |
| 3 | 8/5 | 0.63 | | 0.85 | 2.32 | | 0.37 |
| S. | Fig/Spot | Fe | Zr | O | C | Mn | |
| 1 | 3/ 1 | 0.56 | 9.39 | 44.10 | | | |
| 1 | 4/1 | | | 48.59 | 44.46 | | |
| 1 | 4/ 2 | | | 53.21 | 44.40 | | |
| 2 | 5/1 | 72.3 | | 23.81 | | | |
| 2 | 6/1 | 64.7 | | 26.04 | | | |
| 2 | 6/2 | 0.65 | | 47.93 | 48.90 | | |
| 3 | 7/1 | 73.8 | | 19.62 | | 0.45 | |
| 3 | 7/2 | 74.4 | | 21.66 | | 0.48 | |
| 3 | 8/5 | 67.9 | | 27.14 | | 078 | |

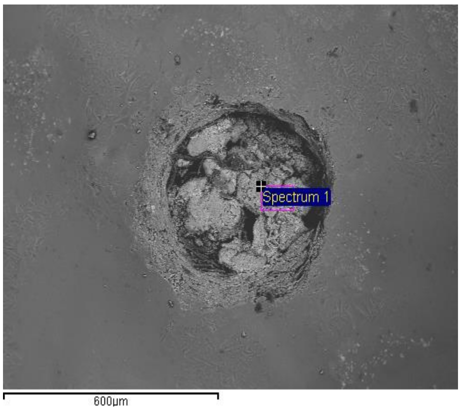

Fig. 5. SEM microphotograph of the Sample 2: round pore filled with dark brown substance and yellow hal

The SEM analysis of the Sample 2 discovered presence of following defect types: round pores were filled with dark-brown substance and surrounded by a yellow halo, another group of round pores were filled with dark brown and black substance, empty pores were present and pores filled with black substance. A defect with dark brown inclusion is presented in Fig. 5. EDS microanalysis of the dark brown matter highlighted the presence of Fe as main element, as well as O (besides Au which originates from the coating used for preparation of the sample). A defect with dark brown and black inclusion is illustrated in Fig. 6. EDS analysis of the middle part of the inclusion (Spectrum 1) pointed out to the presence of Fe, while the fibers near the pore wall mainly contained the carbon (Spectrum 2).

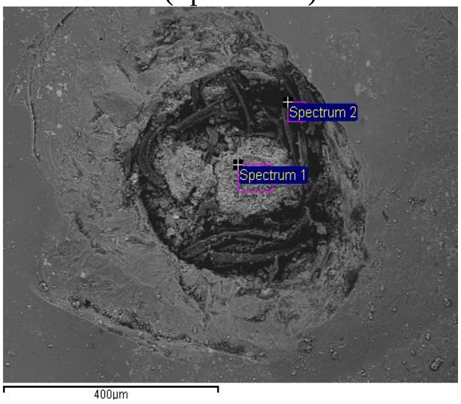

Fig. 6. SEM microphotograph of the Sample 2: round pore filled with dark brown and black substance

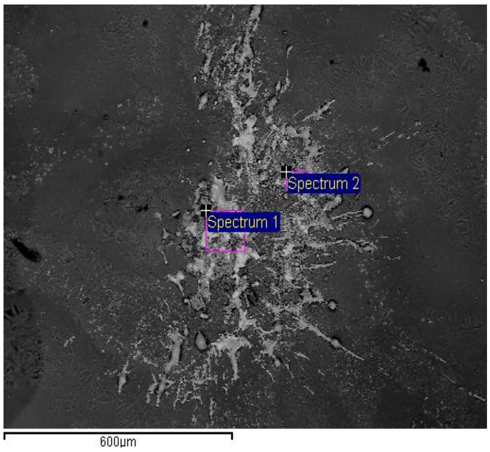

Fig. 7. SEM microphotograph of the superficial defects: dark brown formations of irregular shape

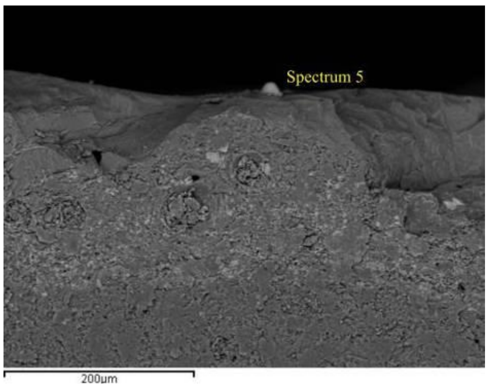

Fig. 8. SEM microphotograph of the cross-section of the tile with dark brown irregular-shaped formations

Based on the SEM recordings of the Sample 3 following defects were identified: formations of the irregularly shaped piles of dark brown substance sizing (0.4–0.8)mm, as well as the empty pores or pores filled with the dark substance. A characteristic dark brown substance of irregularly shaped formation, analyzed by SEM, is presented in Fig. 7. EDS microanalysis of this substance pointed out on the presence of Fe as main element as well as the O (besides Au which originates from the coating used for preparation of the sample). SEM recordings of the piled substance showed that these formations are adhered to the tile surface. It was concluded that pores/voids in the glaze did not appear below described piles. In order to confirm that spark beams were not the cause of voids/pores appearance in the glaze, the analysis of the tile cross section has been performed. SEM microphotograph is given in Fig. 8. EDS microanalysis is provided in the Table 1. These microphotographs also confirm absence of the pore/void and that piled dark brown substance is located only on the surface of the tile.

## 2.2 Defects on surfaces of roof tiles

In order to determine the nature and causes of inhomogeneities on the surface of roof tiles, investigation was conducted on the fired sample (Sample C1) and raw material from which the sample was produced (sample S1). Residue on 63 microns sieve was tested on the raw starting material (Arsenović et al, 2013). Roof tiles have been examined in accordance to the requirements of SRPS EN 1304: 2012. Physical and mechanical properties are tested by the methods defined in the following standards: SRPS EN 538: 2005 Flexural strength test, SRPS EN 539-1: 2011 Impermeability test and SRPS EN 539-2: 2011 Tests for frost resistance. The tests results (Table 2) showed that roof tiles meet the requirements of the standards.

Table 2. Physical and mechanical properties of roof tiles (Sample C1)

| Flexural strength test | | Impermeability test | Tests for frost resistance |
|---|---|---|---|
| Fracture load (N) | | Time elapsed until the first drop fall | 150 cycles |
| Mid. | 1879 | > 20$^h$ | No defects |
| Min. | 1792 | | |

The quality of the visible surface of roof tiles is determined by visual examination, and therefore defects were not observed. After immersion or spraying with water, certain "stains" of color shade that suggest a certain inhomogeneity of the structure of tiles are noticed. These parts, in wich the changes appeared, were cut and submitted to SEM-EDS analysis.

Inhomogeneities on the surface of roof tiles (C1.1 sample) were recorded via SEM at 50x magnification (Fig. 9.). EDS analysis is performed in certain spots. Fig. 10. shows microphotograph pattern of Sample C1.1, with four analyzed surfaces: three surfaces (spectrum 1, 2 and 3) encompass areas with inhomogeneous structure and irregular hairline, while the area designated as a spectrum 4 is homogeneous. EDS analysis results of those areas is given in Table 3. The results indicate an increased content of iron (ranged from 8.46 % to 18.26 %) and manganese (up to 3.89%) in the field with inhomogeneous structure. Homogeneous structure area showed the iron content of 7.58 %, and manganese was not identified.

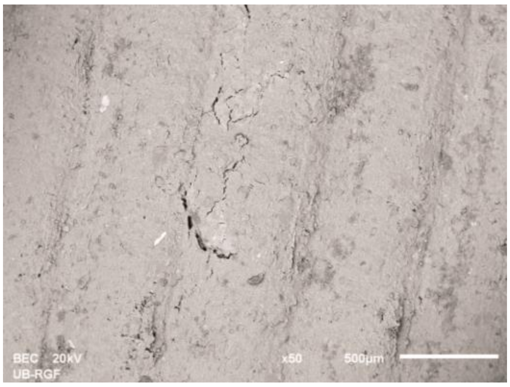


Fig. 9. SEM microphotograph of inhomogeneities on the surface of roof tiles (sample C1.1) at a magnification of 50x

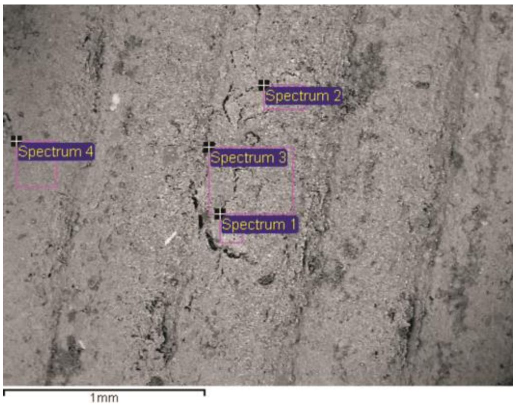


Fig. 10. SEM microphotograph of inhomogeneities on the surface of roof tiles (sample C1.1), areas that were analyzed by EDS

Table 3. EDS microanalysis results of tested roof tiles

| | C1.1 | C1.1 | C1.1 | C1.1 | C1.2 | C1.2 | C1.2 |
|---|---|---|---|---|---|---|---|
| | Sp.1 | Sp.2 | Sp.3 | Sp.4 | Sp.1 | Sp.2 | Sp.3 |
| Na | 0.87 | 0.93 | 0.88 | 0.82 | 0.85 | 0.62 | 1.12 |
| Mg | 1.11 | 1.16 | 1.46 | 1.48 | 0.96 | 1.17 | 1.27 |
| Al | 9.21 | 10.53 | 11.20 | 11.23 | 8.83 | 7.72 | 10.23 |
| Si | 21.49 | 26.70 | 26.99 | 28.29 | 21.85 | 19.38 | 29.22 |
| K | 1.48 | 1.96 | 1.20 | 2.25 | 1.89 | 1.39 | 2.15 |
| Ca | 0.95 | 1.00 | 1.04 | 0.92 | 1.62 | 1.36 | 1.57 |
| Ti | 0.51 | 0.81 | 0.60 | 0.58 | 0.69 | 0.38 | 0.37 |
| Mn | 3.89 | 1.91 | 0.95 | 0.00 | 8.72 | 12.95 | 0.33 |
| Fe | 18.26 | 9.08 | 8.46 | 7.58 | 11.14 | 11.24 | 6.69 |
| O | 42.23 | 45.92 | 46.22 | 46.86 | 43.44 | 41.98 | 47.04 |

Sample C1.2 is also analyzed at higher magnification (100x) and SEM recording is given in Fig. 11. Inhomogeneity is of circular shape, with a diameter of about 1.5 mm. Within and around the grains there are visible microcracks, which give more porous structure in relation to the basic structure of the roof

tile. In Fig. 12, microphotograph pattern of Sample C1.2 is given in three points. Areas that were analyzed (Spectrum 1 and 2) cover an area within the grain. Area designated as a Spectrum 3 contains no inhomogeneities. The results presented in Table 3 indicate an increased content of iron (from 11.14 % to 11.24 %) and manganese (8.72% to 12.95%) within the grain.
The results of roof tiles surface analysis showed that the inhomogeneity is caused by ferruginous-manganese grains larger than 1 mm. In order to determine the nature of grains, the separation of sand fractions from starting raw material is performed. The separation is done by wet sieving using 63 micron sieves. The sieve residue is based on the grain size divided into fractions of 0.063 mm to 0.125 mm, from 0.125 mm to 0.25 mm, from 0.25 mm to 0.5 mm, from 0.5 mm to 1 mm, and of 1 to 4 mm. The sieve residues were analyzed by stereomicroscope.

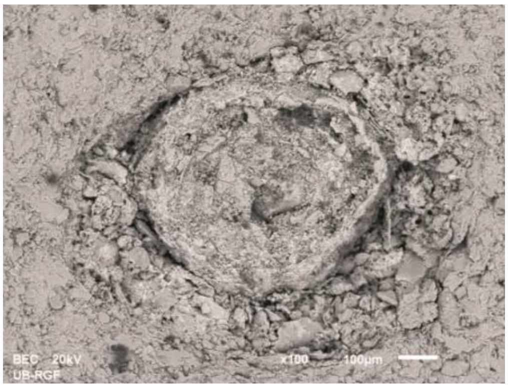

Fig. 11. SEM microphotograph of inhomogeneities on the surface of roof tiles (sample C1.2) at a magnification of 100x

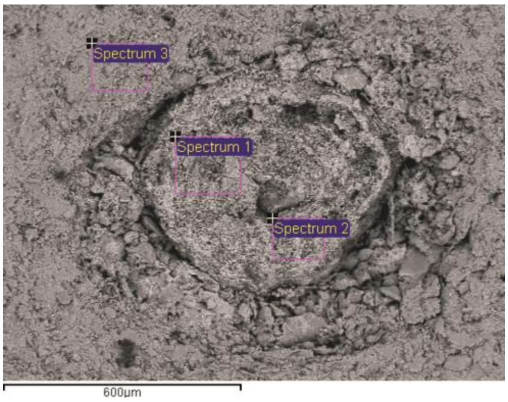

Fig. 12. SEM microphotograph of inhomogeneities on the surface of roof tiles (sample C1.2), areas that were analyzed by EDS

The mineralogical identification of sieved fractions showed the presence of the following minerals (Mudrinić, 1997):
- The (1-4)mm fraction showed white angular quartz grains as the dominant ingredient. Spherical, well-rounded aggregate to kidney-like beans, black and dark brown in color, are metallic minerals that belong to some kind of iron minerals (magnetite, hematite, goethite and martite) with matt gloss. Individual grains show strong ferromagnetic properties.
- The (0.5-1)mm fraction is composed of the same ingredients as the previous fraction.
- The (0.25-0.5)mm fraction showed the same amount of quartz and bowl to kidney-like grain metallic minerals, followed by mica (muscovite and biotite), feldspar and charred parts of plants.
- The 0.125mm to 0.25 mm fraction is composed of mica, quartz, metal-mineral, feldspar and charred parts of plants.
- The smallest fraction (0.125 - 0.063)mm is constructed of mica, quartz and metallic minerals.

When iron minerals are concerned (magnetite, hematite, goethite and martite), ther is the often case that $Fe^{3+}$ is replaced with $Mn^{3+}$, or other metals. It should be noted that the main characteristics of magnetite, after which it deffers from other similar minerals, are strong magnetism and high hardness (Mohs hardness 6) (Janjić and Ristić, 1989). In the process of pressing of roof tiles, larger grains of magnetite behave like quartz grains, they "rip the surface". However, in places of metallic grains, during firing of roof tiles, porous structure is obtained, which is not the case with quartz grains that remain compact. As an illustration, SEM micrograph of quartz grains on the surface of Sample C1.3 is given (Fig. 13).

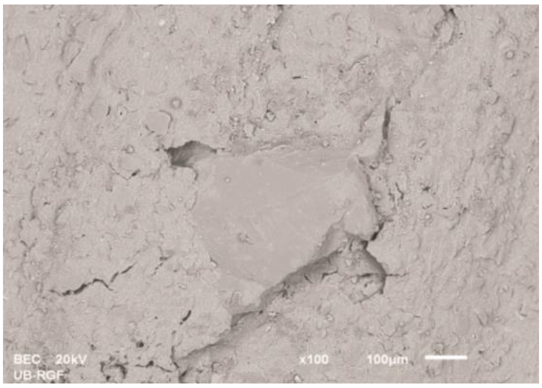

Fig. 13. SEM microphotograph of inhomogeneities on the surface of tile that caused quartz grain (Sample C1.3)

## 3. CONCLUSIONS

Tested samples of glazed ceramic tiles showed surface defects which appeared as circular pores - empty or filled in inclusion. The pores are found in the surface layer / glaze. In the sample that was not previously installed in a building, the surface layer / glaze contained empty pores and pores filled with a black substance that EDS analysis identified as carbon. According to the requirements of standard SRPS EN ISO 10545-2: 2012, this phenomenon does not affect the surface quality. Carbon probably originates from organic impurities entered through the raw materials used to make the glaze. Because of the incomplete combustion in the firing process, carbon is trapped in a glaze or withiin open pores on the surface of the glaze. In the case of the tiles removed from the façade, glazes contained the pores filled with dark brown substance with a yellow halo, pores filled with dark brown and black matter, pores filled with black matter alone and empty pores. According to the requirements of the standard, appearance of alike pores affect the quality of the visible surface of the tiles, which are then defined as ceramic tiles with defect. EDS analysis of clusters of dark-brown color in the pores showed the presence of Fe. The apperiance of the halo of yellow rust is evident around these inclusions. Also, the pores with dark brown and black inclusions were present. EDS microanalysis of the central part of these inclusions showed the presence of iron, and the fibrous part of the inclusions dominantly contained elemental C. Also, empty pores and pores filled with dark matter (carbon) were present. Iron is probably imported with the raw materials used for glaze as impurities or is inadvertently applied to the surface of the tiles (due to welding and grinding) in the production process and before the firing process. Pores filled with dark brown material occured in places where Fe impurities appeared during the firing process. The pores of the same shape filled with a ferruginous matter and carbon fiber matter also appeared. The form of full and empty pores is almost identical, indicating that they arose during the firing process. The possibility that defects of ferrous nature occured due to the grinding process near the surface of the tiles during installation is therefore excluded. Experimental probe is done which confirmed that the "jet sparks" from grinding do not cause the formation of pores in the glaze, but that clumps of dark-brown matter bonded to the surface of the tiles. The cause of inhomogeneities on the surface of roof tiles is a local phenomenon of porous structure formation due to microcracks that cause metallic grains which are entered with the starting raw material. The grains were spherical, well-rounded to kidney-like shaped, black and dark brown in color. They belong to some of iron minerals (magnetite, hematite, goethite and/ or martite) mat gloss. The individual grains, particularly magnetite, have strong ferromagnetic properties, and high hardness. Larger grains after firing of roof tiles give a certain inhomogeneity of surface, in the form of micro cracks. Such a surface is manifested as a "blotchy" after soaking or spraying with water.

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