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Self-Cleaning Layers of TiO_2 on the Brick Surfaces

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Abstract

A deposition method of TiO_2 layers on the surface of commercial bricks has been proposed. X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to determine chemical and phase compositions as well as microstructure of the fabricated layers. In spite of high temperature heating, comparable to that needed to firing raw bricks (above 1000 °C) the deposited TiO_2, as the rutile phase, remains on the brick surface, and then it is enable to photocatalytic degradation of typical contaminants of the building surface playing role of a self-cleaning agent.
Słowa kluczowe: TiO_2, Self-cleaning layer, Ceramic brick, Photocatalysis

SAMOCZYSZCZĄCE WARSTWY TiO_2 NA POWIERZCHNIACH CEGIEŁ

Opracowano metodę formowania warstw TiO_2 na powierzchni cegieł. Dyfrakcyjna analiza rentgenowska (XRD), elektronowa mikroskopia skaningowa (SEM) oraz rentgenowska mikrosonda (EDS) zostały użyte do określenia składu chemicznego i fazowego oraz mikrostruktury naniesionych warstw. Pomimo warunków wysokotemperaturowego wygrzewania, porównywalnego do tych jakie stosowane są podczas wypalania surowych cegieł (powyżej 1000 °C), nałożone warstwy TiO_2 w formie rutylu, pozostają na powierzchni cegieł i są w stanie degradować typowe zanieczyszczenia, na drodze fotokatalitycznych procesów, na powierzchni budynków, pełniąc rolę warstw samoczyszczących.
Keywords: TiO_2, warstwa samoczyszcząca, cegła ceramiczna, fotokataliza

1. Introduction

Photocatalytic degradation of environmental contaminants has been studied during past four decades. In 1972 Fujishima and Honda [1] discovered photoinduced water cleavage on an electrochemical cell involving the single-crystalline TiO_2 electrode. Since that time hundreds of research papers and monographs have been published describing application of TiO_2-based materials as photoelectrodes [2, 3], photocatalysts for degradation of water pollutants [4, 5], air pollutants [4, 6], self cleaning surfaces [6, 7] and anti-bacterial coatings [8]. All mentioned processes are based on light-stimulated intrinsic electronic ionization occurring in the semiconductor:

$$h\nu \leftrightarrow e' + h^{\bullet}, \quad (1)$$

where $h\nu$ is absorbed photon energy, e' and $h^{\bullet}$ denote electron and electron hole in the conduction and valence bands, respectively.

Both formed electrons and holes are powerful reduction and oxidation agents enable to proceed redox reactions leading to complete decomposition of many organic contaminants. Moreover, the light-induced super hydrophilic phenomenon occurring in TiO_2 leads to self-cleaning surfaces [7]. If the building material surface coated with a thin layer of TiO_2 is illuminated by solar light the degradation of grease, dirt and other organic contaminants occurs, and the decomposition products can be easily swept away by e.g. rain water.

Many companies have been trying to develop self-cleaning surfaces, especially for the surfaces of building facades (windows and walls). One approach was based on making these surfaces highly hydrophilic so that a stream of water would be able to remove stains caused by organic contaminants. In order to get this process easier the use of surfactants has been proposed. This solution is difficult to succeed due to problems with lack of coating durability, hardness and weather resistance. In contrast, the TiO_2 layer can maintain hydrophilic properties for long time. Moreover, taking into account non-toxicity, chemical stability and low prices of TiO_2 the use of the material to produce self-cleaning surfaces seems to be fully justified.

The purpose of this report is the preliminary study of the method of formation self cleaning surfaces on the surfaces of building materials such as typical ceramic bricks.

2. Experimental

2.1 Materials and preparation of surfaces

Two different series of brick-samples were the object of studies: (i) raw bricks, (ii) fired bricks. Surfaces of both raw and fired bricks were cleaned using a scrubbing-brush.

2.2. Deposition of TiO_2 layers

2.2.1. Preparation of Ti containing paint

Titanium(IV) isopropoxide, TIP, (Aldrich) was used as the titanium organometallic precursor. Two liquid solutions were prepared:

– Solution 1: 30 ml of TIP was mixed with 23.2 ml of absolute ethanol by dropping in an ice bath.
– Solution 2: 23.2 ml of ethanol + 2 ml HCl (35 weight%) + 1.8 ml water. The solution was mixed in an ice bath.

10 ml of the solution 1 and 1 ml of the solution 2 were extensively stirred for 10 minutes, then 7 ml of ethanol was added. Obtained sol was stored at -6 °C.

2.2.2. Deposition of sol layers

The sol was deposited on the fired brick surfaces (samples A, B and C) by means of painting. The layers were dried at room temperature during 24 hours, and then calcinated following the conditions given in Table 1.

2.3. Firing of bricks

Raw bricks with deposited layers of sol (samples D and E) were fired in an electrical furnace according to temperature-time characteristics presented in Fig. 1. Chemical composition of the material (clay) taken to the preparation of specimens was typical to raw materials used in production of bricks in brickfields. Also, the conditions of firing were similar to that occurring commonly in brick kilns.

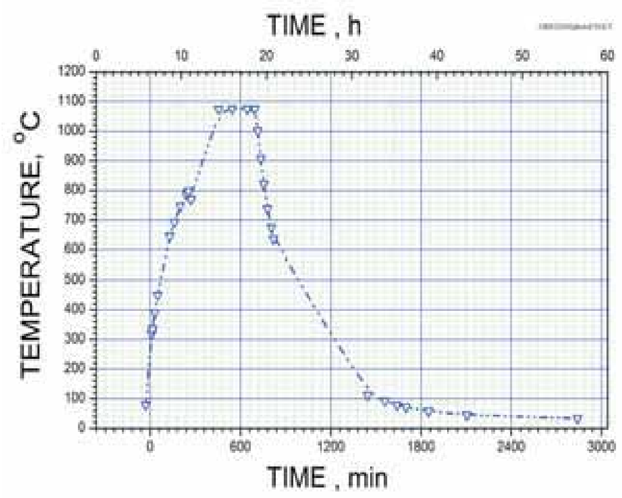


Fig. 1. Firing program of raw bricks with deposited layer of Ti-sol.

Table 1. Conditions of calcination process.

No	Carrier	Symbol of sample	Temperature [°C]	Time [h]
1.	Raw dry brick	D	1050*)	3
2.	Raw dry pavement brick	E	1050*)	3
3.	Fired brick face	A	100	3
4.	Fired brick face	B	200	3
5	Fired brick face	C	300	3

*) for firing schedule see Fig. 1.

3. Results and Discussion

3.1. XRD analysis

The X-ray diffraction analysis (XRD, Philips X'Pert with CuK_α radiation within the 2θ range 10-90° with a scan rate of 0.008°/s) was used to determine the phase composition of the surface layer of fired materials.

Table 4. EDS results for the brick surfaces shown in Fig. 6.

Sample	Place of analysis	Ratio of intensities in respect to Si K_α				
		Ti K_α	O K_α	C K_α	K_αCa	Al K_α
A (Fig. 6a)	1	0.03	0.21	0.19	0.02	0.11
	2	0.09	0.16	0.18	0.00	0.06
	3	0.26	0.63	0.27	0.14	0.33
B (Fig. 6b)	1	0.05	0.57	0.21	0.33	0.11
	2	3.94	0.54	0.34	0.23	0.11
	3	0.03	0.25	0.12	0.10	0.02
C (Fig. 6c)	1	0.07	0.40	0.43	0.05	1.06
	2	1.05	0.72	0.70	0.06	0.69
D (Fig. 6d)	1	1.75	0.51	0.62	0.10	0.21
	2	0.26	0.16	0.24	0.04	0.20
	3	0.26	0.16	0.25	0.03	0.19
E (Fig. 6e)	1	0.07	0.85	0.34	0.11	0.66
	2	1.46	1.33	0.68	0.59	0.53
	3	5.96	0.80	1.04	0.38	0.76

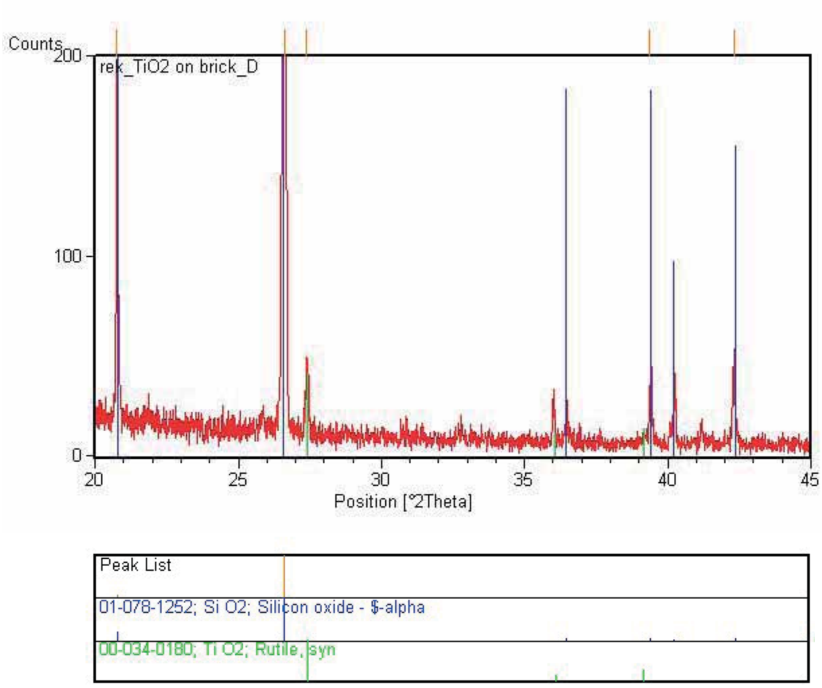


Fig. 2. XRD pattern of the layer on the brick D.

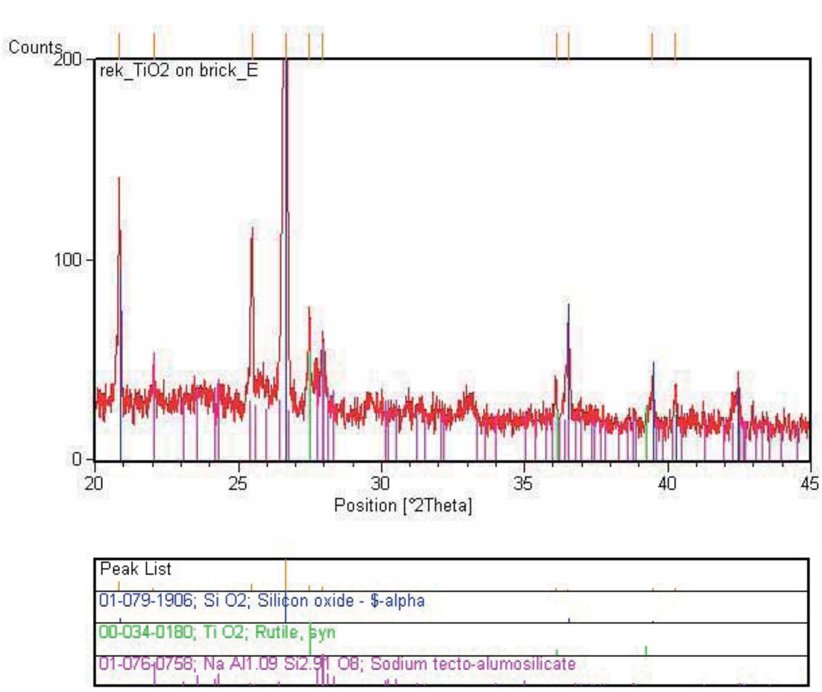


Fig. 3. XRD pattern of the layer on the brick E.

Table 2. Average TiO_2 grain sizes determined from SEM analysis.

Sample	Grain size [μm]
A	0.2 – 0.6
B	0.2 – 0.9
C	0.3 – 0.4
D	0.2 – 1.2
E	0.2 – 1.3

Figs. 2 and 3 illustrate typical XRD patterns of fired specimens. Apart of main brick components such as silica, sodium tecto-alumosilicate phases the reflexes related to the rutile phase are present in the pattern.

3.2. SEM observations of microstructure

Scanning electron microscopy (SEM, FEI Nova NanoSEM microscope) studies were performed to determine the microstructure of the formed layers. Figs. 4 and 5 show typical micrographs of the surfaces. According to the presented micrographs, the microstructures of the used materials differ substantially among each other. The observed TiO_2 grains exhibit uniform shapes. The grain sizes are collected in Table 2. Also, irregular pores are well visible on the micrographs.

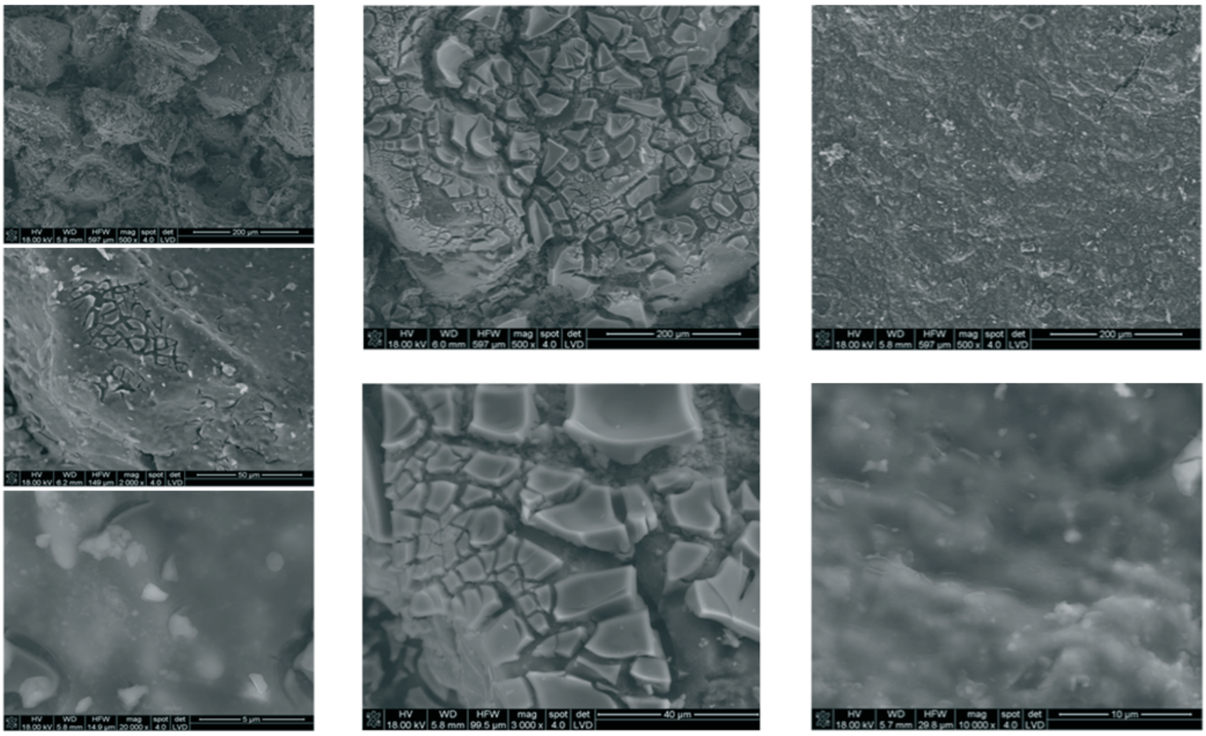
3.3. EDS analysis

The most important aim of this work was the elaboration of the deposition method of titania layers on the brick surfaces which remain stable after the firing procedure typical for industrial processes occurring in a brick kiln. In order to monitor the presence of titania on the fired brick surfaces the EDS analysis was used. Fig. 6 shows the places on the brick surfaces taken to the EDS analysis. Depending on the analyzed area the distribution of main elements concentration changes. However, the reflexes coming from titanium are visible in all spectra. For qualitative determination of titanium and other main elements, the relative intensities of the reflexes expressed as ratios of the heights relaxes in respect to the Si Kα (main component of all samples) were used. The results are presented in Table 4.

Summarizing, we have successfully prepared TiO_2 layers on the brick surfaces which can absorb visible light and work efficiently as photocatalysts for the degradation of typical contaminants.

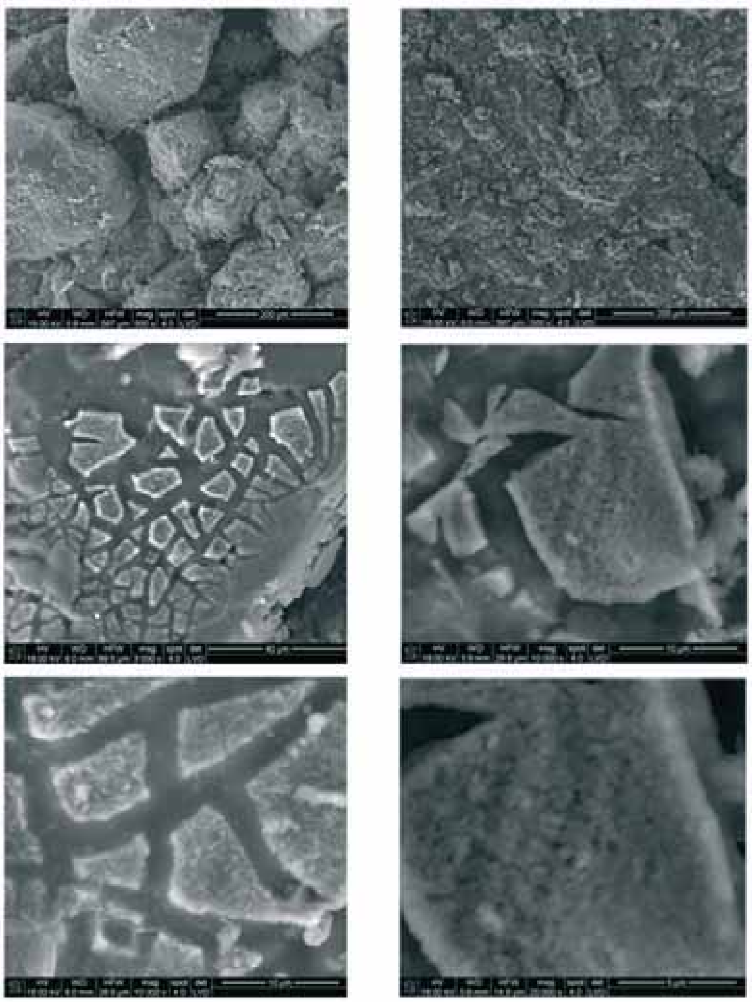
4. Conclusions

For the case of layers applied on fired bricks (samples A, B, and C), the TiO_2 non-continuous layer was found (temperature of second heat treatment ≤ 200 °C). Taking into account low temperature of the heat treatment of these samples the TiO_2 phase should be in the form of anatase.



a) b) c)

Fig. 4. SEM micrographs of brick surfaces: a) brick A, b) brick B, c) brick C.



a) b)

Fig. 5. SEM micrographs of brick surfaces: a) brick D, b) brick E.

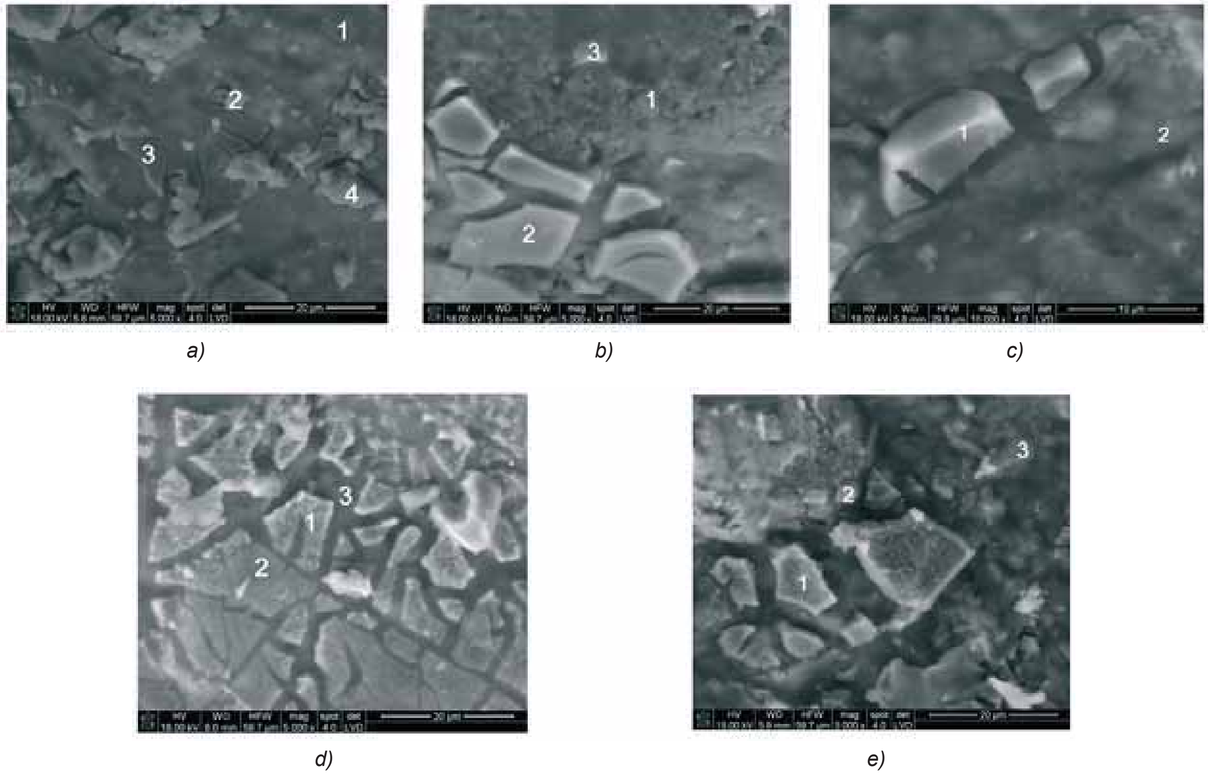


Fig. 6. SEM micrographs of brick surfaces with marked places of EDS analysis: a) brick A, b) brick B, c) brick C), d) brick D, and e) brick E.

For the case of sol applied on bricks before firing (samples D and E) the TiO_2 (rutile) layer was found, due to the firing temperature.

The preliminary study seems to be promising, in particular for layers applied on fired bricks. More detailed studies of processing parameters, adhesion and catalytic properties are necessary. Future work will deal with studies of photocatalytic decomposition of the typical environmental contaminants such as dirt, grease, oil, and other stain materials on the brick surfaces covered with TiO_2 layers.

Acknowledgements

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