CONTROLLED CRYSTALLISATION OF TiO_2 IN ALKALI-BOROSILICATE GLASS AND ITS BACTERICIDAL PROPERTIES

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The influence of thermal processing on TiO_2 crystallisation in alkali-borosilicate glass was investigated applying differential thermal analysis, X-ray diffraction analysis and electron microscopy. The surfaces of the samples prepared by both volume and surface TiO_2 crystallisation were evaluated from the viewpoint of their respective bactericidal properties. A polycrystalline material with anatase forming the only crystalline phase with crystal size ranging from 0.01 to 0.5 μm, was prepared by controlled, volume glass crystallisation. The bactericidal effect was demonstrated on fracture surfaces of a mechanically ground sample of crystallized glass.

INTRODUCTION

Titanium dioxide is a well-known photocatalyst whose oxidative properties manifest after UV irradiation acts as an efficient environment-friendly bactericidal agent applicable also for the purpose of removing harmful substances from liquid and gas compounds by photocatalytic oxidation [1, 2]. In practice, either TiO_2 suspensions are used or TiO_2 is affixed to the surface of a suitable solid carrier, using TiO_2 as a photocatalyst. TiO_2 is applied to the carrier, e.g., by means of powder spraying or the sol-gel method [3, 4]. The TiO_2 crystals are most often anchored to the solid substrate by means of thermal fixation, preferably on the surface of a ceramic or glass carrier (boards, tubes, balls or fibres) [2,5]. An alternative method of preparing the glass matrix with scattered TiO_2 crystals is controlled glass crystallisation [6]. Applying the method of controlled crystallisation of glass of a suitable composition, it is possible to prepare a polycrystalline material with TiO_2 forming the only crystalline phase. The examples of suitable materials include, e.g., R_2O-B_2O_3-SiO_2-(TiO_2) system glasses used for the preparation of TiO_2-based enamels [7]. Selecting the method of parent glass thermal processing, it is possible to control the kind of crystallising phase, size of crystals or the utilisation of surface or volume nucleation in the course of the crystallisation process, i.e. the factors influencing the photocatalytic activity of TiO_2. This study deals with the effect of thermal processing on TiO_2 crystallisation in alkali-borosilicate glass and its resulting, photocatalytic properties.

EXPERIMENTAL PART

Preparation of glass and applied methods

The glass (composition: 39.5% SiO_2, 21% TiO_2, 16% B_2O_3, 9.5% Na_2O, 5%K_2O, 1.5% P_2O_5, 1% Li_2O and 6.5% F) was prepared by melting the appropriate amounts of reagent-grade raw materials. The melting process was carried out using a platinum crucible kept in an electric furnace at a temperature of 1250°C for a period of 4 hours. Approx 250 g of melt were poured on a metal board so as to cool down quickly. After quenching the melt, the glass was crushed into powder and remelted to attain improved homogeneity. Subsequently the melt was poured into a metal mold to obtain sticks 1-2 cm in diameter. Grit fractions with particle sizes of < 0.056, 0.056-0.507, 0.507-1, and > 1 mm were prepared by crushing the melted glass and sieving. The grit was used for the DTA measurement.

The glass crystallisation process was observed applying the differential thermal analysis method (Linseis L62 DTA). The respective crystalline phases were identified applying X-ray diffraction analysis (XRD 300, Rich. Seifert & Co. GmbH.) using powdered or solid samples. The surfaces of the respective samples were observed using a scanning electron microscope SEM (JEOL 733 Super Probe) with an energy dispersion X-ray analyser (EDS).

Bactericidal efficiency evaluation

The bactericidal efficiency of TiO_2 was evaluated by determining the decrease of the number of live microorganisms whose initial concentration was known and that were in contact with the sample under evaluation exposed to the light of a given intensity for a given period of time. The intensity of the radiation used was measured within the range of 310-400 nm using a Minolta UM-10 UV radiometer. The G-bacterium *Escherichia coli*-DH 5α of the collection kept by the Enzyme Technologies Laboratory of the Institute of Microbiology, Academy of Sciences of the Czech Republic, were used for the evaluation. The bacteria were cultured on Chromocult coliformen agar (Merck) at 37°C.

A microbial suspension with known cell concentration was prepared in accordance with McFarland's scale [8]. Before each measurement the cell concentration was checked by means of plating the microorganisms on dishes containing a selective agar medium. The initial concentrations of the bacteria were in the range of 10^6 to 10^7 cells/ml. To evaluate the bactericidal efficiency a certain volume (0.2 ml) of the contaminating cell suspension was applied to the surface of the sample under investigation. The sample surface with cell suspension was covered by a sterile polyethylene foil (4 cm^2), so that the surface of the sample was contaminated at an average density of 10^6 cells/4 cm^2. The sample located in a sterile laminar box on a Petri dish was then exposed to the light emitted by a discharge tube (light intensity: 4.1 μW/cm^2 at a wavelength of 310-400 nm). After a given period of exposure the microorganisms were flushed from the sample surface into 10 ml of sterile physiological saline. Following membrane filtration, the filter was put on the selective agar soil and the number of cell colonies corresponding to the number of surviving microorganisms on the surface of the sample under observation determined after 24 hours. All the measurements were compared with parallel measurements of a control substrate showing no bactericidal effect.

RESULTS AND DISCUSSION

In controlled glass crystallisation, crystallisation initiated by either volume or surface nucleation may occur. In the case of volume crystallisation, the crystals of every crystal particle grow three-dimensionally on nuclei scattered within the glass. In the case of surface crystallisation, nuclei are formed only on the surface (i.e. on the boundary between the vessel or air and the glass), and crystals grow from the surface to the inside of the glass one-dimensionally. The thermal dependence of nucleation rates and crystal growth shown by the respective phases determine the crystallisation kinetics (crystallisation properties) that can be controlled by modifying the conditions of thermal processing.

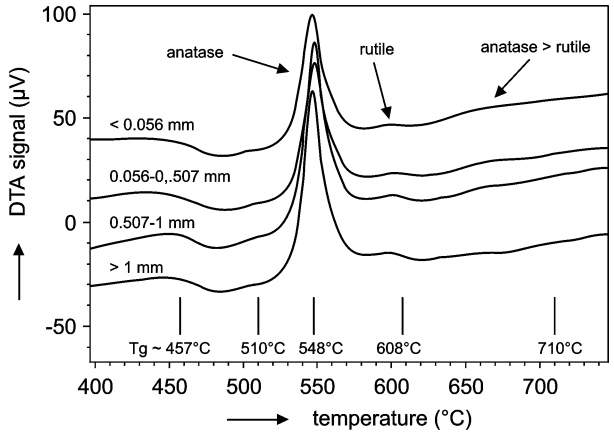

Figure 1. DTA glass lines of the samples with different particle sizes (< 0.056, 0.056-0.507, 0.507-1, > 1mm) heated at the rate of 5K/min.

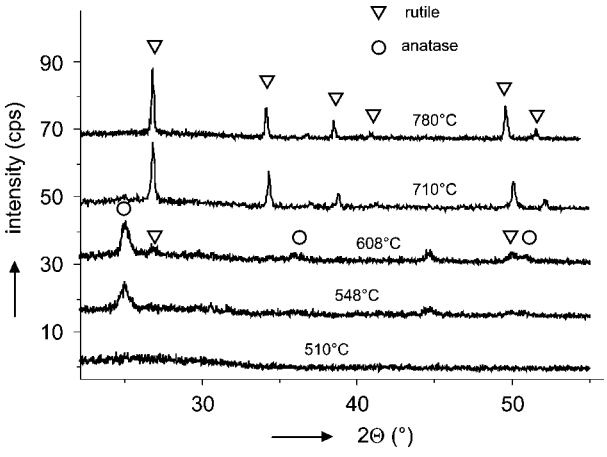

Figure 2. X-ray diffraction analysis (XRD patterns) of the crushed glass samples (0.056-0.507 mm) heated at the rate of 5K/min and cooled down quickly after reaching the defined temperatures (510, 548, 609, 710 and 780°C).

Volume crystallisation

The differential thermal analysis (DTA) was applied to evaluate the crystallisation properties of the glass under investigation. When crushed glass is heated at a constant rate of 5 K/min (figure 1), anatase is separated first, with rutile beginning to crystallise with increasing temperature as indicated by X-ray diffraction analysis carried out on the samples of crushed glass (0.056-0.507 mm) heated at a rate of 5 K/min and cooled down quickly after reaching the target temperatures of 510, 548, 609, 710 and 780°C (figure 2). If the temperature exceeds 608°C, the metastable anatase phase inverts to rutile, with rutile identified as the only crystalline phase once the temperature reaches 710°C.

To evaluate the course of surface and volume crystallisation, samples of various particle sizes were measured (figure 1). As previously demonstrated [9, 10], the initial concentration of nuclei in glass is proportional to the reciprocal value of the temperature of the top of the DTA crystallisation peak ($1/T_p$). In the case of surface nucleation, the temperature of the top of the DTA crystallisation peak (T_p) shifts towards relatively lower values, with the number of nuclei growing with increasing specific surface area of the sample. On the other hand, in the case of distinct volume crystallisation with negligible surface crystallisation, T_p is independent of the sample surface area.

The DTA measurements of samples with various grain sizes (< 0.056, 0.056-0.507, 0.507-1, > 1 mm) indicate that both the anatase (T_p = 546.4-547.4) and rutile (T_p = 599.6-601.9) nucleations are predominantly of the volume type.

A faint peak in the area of the temperatures ranging from 630 to 700°C corresponding with the transition of anatase to rutile becomes more distinct with the decreasing grain size of the samples and shifts towards lower temperatures, indicating that the transition is surface influenced.

The surfaces of compact samples heat treated at temperatures of 410, 540 and 760°C for 20 minutes were observed with an electron microscope and electron microprobe. Unless etched, the samples showed smooth surfaces (figure 3a). After completing the observation with an electron microscope, the samples were treated by immersing in 1% HF for 2 seconds and washing in distilled water and acetone. The sample heated to 410°C showed a typical microstructure of metastable separation in the liquid phase (figure 3b) and according to the X-ray diffraction analysis, the sample was amorphous. Anatase and a small amount of rutile crystallised at the temperature of 540°C (figure 3c). The sample processed at 760°C showed crystals (0.1-1.0 μm) protruding from the glass matrix identified as rutile according to their chemical composition and X-ray diffraction analysis (figure 3d).

Anatase phase nucleation

The anatase crystallisation mechanism was investigated using DTA on the basis of determining the volume fraction of crystallising anatase while heating the glass sample at constant rates of 3, 4, 5 and 6 K/min (figure 4). The degree of transition ($x = S_T/S_o$) at the selected temperature for various heating rates was determined from the ratio of the partial (S_T) and total (S_o) surface of the exothermic peak as shown in figure 4.

An equation expressing the volume fraction, x, of crystals precipitating in the glass heated at a constant rate, r, was derived [11] as a function of temperature and heating rate

$$\log(-\ln(1-x)) = -n \log(r) - m\,E/2.3RT + \text{const} \qquad (1)$$

where E is the activation energy for crystal growth and n and m are numerical factors depending on the mechanism of crystallisation (table 2).

Plotting the $\log(-\ln(1-x))$ against $\log(r)$ values for the respective temperatures, we obtained the lines shown in figure 5. According to equation (1), the gradient of these lines represents the $-n$ values determined by applying the least squares method to the experimental points, which yields the following values: n = 3.7 (515°C), 3.8 (520°C), 3.5 (525°C), 3.7 (530°C) and 3.7 (535°C). The n values approaching 4 indicate dominant volume nucleation of the anatase phase with three-dimensional crystal growth.

Table 1. Temperatures of the exothermic peak maxima (T_p) on DTA curves (figure 1) for various grain sizes of crushed glass samples determined using the Linseis L62 DTA evaluation program.

Grain size	T_p (°C)		
	Anatase	Rutile	Anatase⇨Rutile
> 1 mm	546.9	599.6	662.7
0.507-1 mm	547.4	601.6	661.4
0.056-0.507 mm	547.4	601.3	659.8
< 0.056 mm	546.4	601.9	656.9

Table 2. Values of n and m for various crystallisation mechanisms [11].

Mechanism	n	m
Bulk nucleation		
Three-dimensional growth	4	3
Two-dimensional growth	3	2
One-dimensional growth	2	1
Surface nucleation	1	1

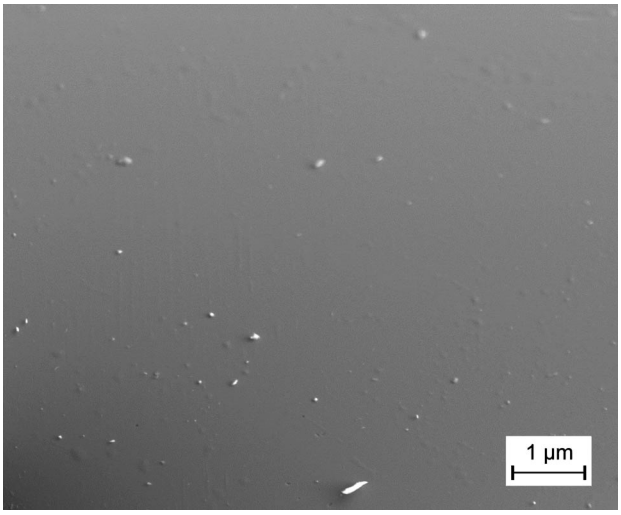

Figure 3a. SEM image of the surface of non-etched glass heated to 540°C for a period of 20 minutes.

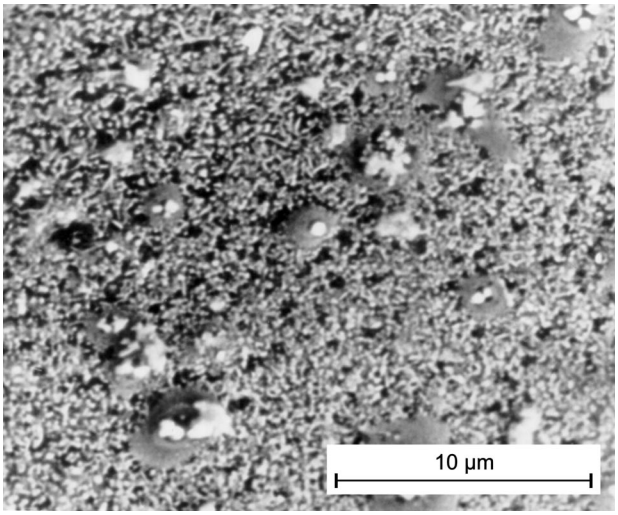

Figure 3c. SEM image of the glass heated to 540°C for a period of 20 minutes and etched with 2% HF.

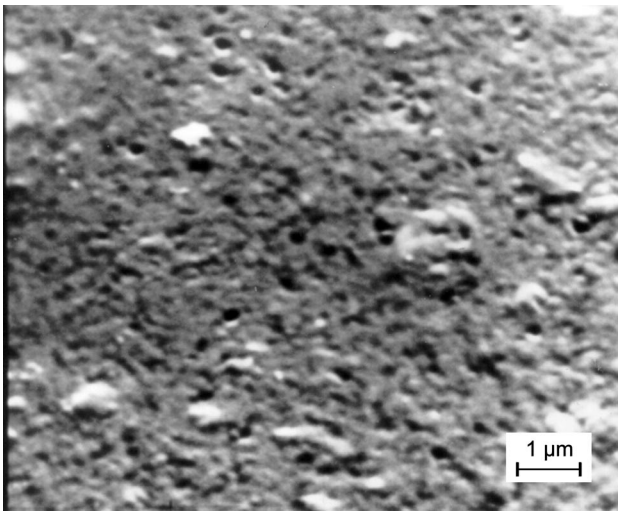

Figure 3b. SEM image of the glass heated to 510°C for a period of 20 minutes and etched with 2% HF showing the metastable liquid - phase separation microstructure.

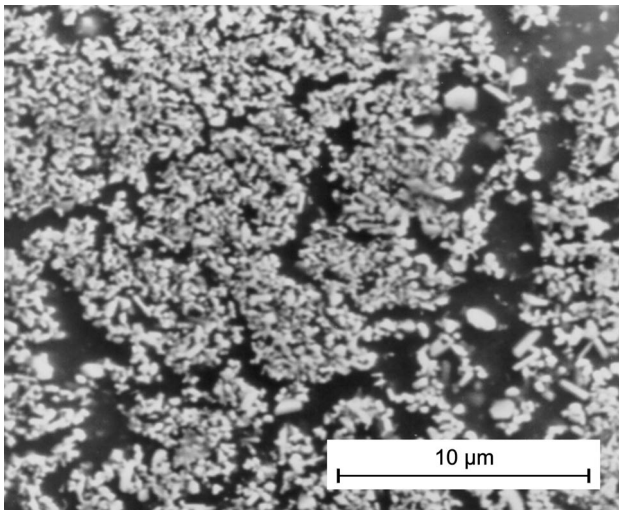

Figure 3d. SEM image of the glass heated to 760°C for a period of 20 minutes and etched with 2% HF.

To determine the dependence of the nucleation rate on temperature, the glass samples were heated to the respective nucleation temperatures T_n = 410, 450, 475, 490 and 510°C for a period of 10 minutes before performing the DTA measurement. As mentioned above [9, 10], the initial concentration of nuclei in glass is proportional to the reciprocal value of the temperature of the DTA crystallisation peak maximum, $(1/T_p)$. The reciprocal values of the temperatures corresponding to the crystallisation peak maximum (T_p) obtained from the DTA measurement for the glass samples nucleated at various T_n temperatures are summarised in figure 6. The maximum nucleation rate temperature of anatase determined from the dependence relation approached the value of 490°C.

Surface crystallisation

Surface crystallisation of glass was observed by the application of the controlled melt cooling method. The parent glass was melted in a platinum crucible at a temperature exceeding the liquidus temperature (1250°C) and cooled down to 850°C (800°C, 750°C), kept at that temperature for 10 minutes and then cooled down quickly in air. The solid samples of crystalline glass removed from the platinum crucibles were observed with an electron microscopes and X-ray diffraction analysis was applied. The crystallisation patterns were significantly different on the sample surface (glass/platinum, glass/air) and inside the sample. The resulting crystallisation patterns are summarised in table 3. The

rutile surface crystallised on the glass/platinum boundary at all the temperatures applied (850°C, 800°C and 750°C; figure 7). The diffraction patterns exhibited a strong texture, as the layer grew mostly along the (110) orientation of the rutile crystal. The diffraction peak (110) intensity ten times higher than the other diffraction lines compared with the diffractogram of pure powdered rutile demonstrated the preferential nucleation and the growth of the rutile phase along the (110) orientation on the glass/platinum interface (figure 9, figure 2).

The rutile and anatase crystallisation on the glass/air boundary along with a non-identified crystalline phase were identified solely at the temperature of 750°C (figure 9, figure 8). The sample also showed a deep opacification at that temperature, indicating metastable segregation development in the liquid phase.

Bactericidal effect determination

The bactericidal effect of the crystallised glass was verified using three characteristic samples (table 4). Sample A was prepared by volume crystallisation applying the two-step thermal processing method. The glass sample was heated to a temperature corresponding with the maximum nucleation rate (490°C) and kept at that temperature for 3 hours. Then the temperature was increased to 545°C and the sample kept at that temperature for 3 hours. Applying X-ray diffraction analysis, anatase was identified as the only crystalline phase with crystal size ranging from 0.01 to 0.5 μm, which was also identified by a significant broadening of the diffracted lines. Before carrying out the measurement, the sample was ground off to a depth of ca 1 mm (Figure 10). Sample B was prepared by thermal processing of the parent glass at a temperature of 790°C for a period of 20 minutes. Before carrying out the measurement, the sample surface was immersed in 1% HF for a period of 2 seconds and washed with distilled water and acetone. The sample surface showed only rutile crystals of sizes ranging from 0.1 to 1.0 μm protruding from the glass matrix (figure 3d). Sample C was prepared by heterogeneous nucleation on the platinum surface during the controlled cooling of the melt. The melt was cooled down to 800°C and kept on a platinum pad for 10 minutes and then cooled down quickly in air. Removing the platinum pad, a surface with a crystallised rutile layer was obtained with the preferential (101) orientation of the rutile crystals parallel with the sample surface (figure 7).

To evaluate the bactericidal efficiency, the *Escherichia coli*-DH 5a bacteria of the initial concentration of 5×106 cells/ml were used. The sample surface of 4 cm^2 was coated with 0.2 ml of microbial suspension. In the course of the contact period of 60 minutes, the samples were exposed to the light emitted by a discharge tube (light intensity: 4.1 μW/cm^2 at a wavelength of 310-400 nm). The number of colonies corresponding to the number of surviving microorganisms were determined after 24 hours according to the procedure mentioned above. The numbers of colonies after the expiration period (table 4) represent the average values of two parallel measurements. Checks were performed analogously with glass samples of the same size and surface roughness showing no bactericidal effect. The measurement

Table 3. Samples crystallisation patterns for the melt cooled down to 850°C, 800°C and 750°C.

Crystallisation temperature	Phases formed on the platinum/glass boundary	Phases formed inside the sample	Phases formed on the air/glass boundary
850°C	Rutile	Amorphous, transparent glass	Amorphous
800°C	Rutile	Amorphous, transparent glass	Non-identified phase d = 0.332 nm
750°C	Rutile (anatase)	Amorphous, opalescent	Rutile, anatase, non-identified phase d = 0.311 nm

Table 4. Bactericidal effect of crystallised samples of glass.

Sample	Number of cell colonies after the expiration of the contact period (60 minutes)	Initial concentration (cells/4 cm^2)
A	9	10^6
B	UA	10^6
C	40	10^6
Control sample	UA	10^6

UA - uncountable amount (>>10^3)

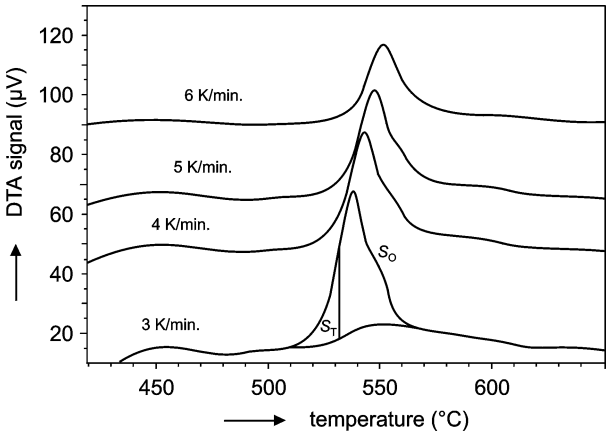

Figure 4. DTA glass crystallisation curves for heating rates of r = 3, 4, 5 and 6 K/min. The method of calculating the degree of transition (x = S_T/S_o) at the given temperature is demonstrated.

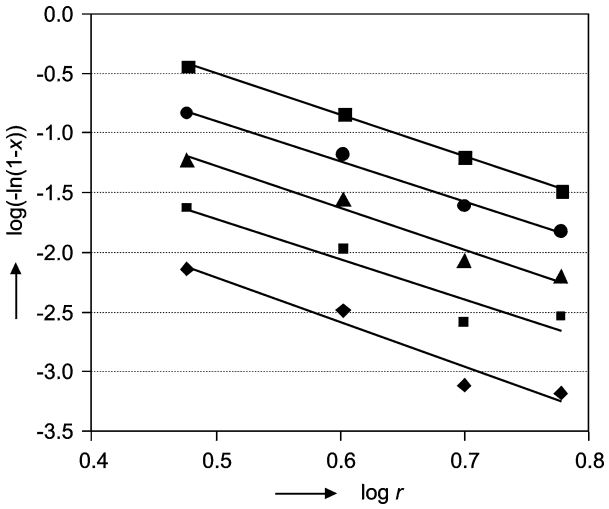

Figure 5. Plots of the log (-ln(1-x)) and log(r) values for temperatures of 515, 520, 525, 530 and 535°C.

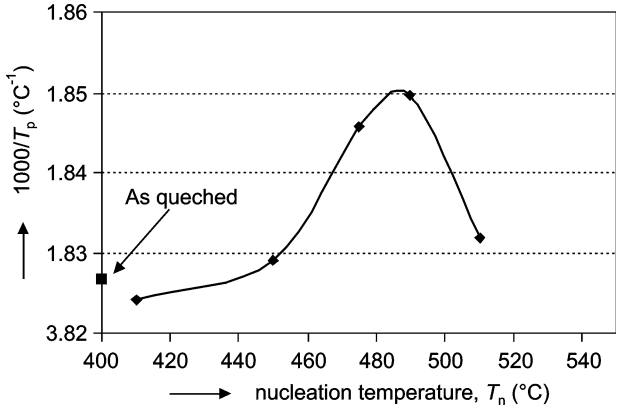

Figure 6. Reciprocal values of temperatures corresponding to the DTA crystallisation peak maxima (T_p) as a function of the nucleation temperature at the heating rate of 5 K/min.

results (table 4) obtained with sample A indicate the bactericidal properties of the sample that may be related to the presence of the anatase modification of TiO_2 in the form of small crystals enhancing the effects of photocatalysis to a significant degree [12]. The bactericidal activity observed with sample C may be influenced by the preferential orientation of crystals on the sample surface that promotes photocatalysis significantly as observed with TiO_2 photocatalytic coats [3]. The bactericidal effect was not observed with sample B, which was prepared by etching the sample surface in HF. A possible explanation is that the products of the interaction of the hydrofluoric acid with the sample surface inhibit the photocatalytic activity of TiO_2.

CONCLUSION

Thermal processing methods applicable to the crystallisation of TiO_2 as the sole crystalline phase in alkali-borosilicate glass by volume and surface nucleation have been developed. A polycrystalline material with anatase (crystal size: 0.01-0.5 mm) forming the only crystalline phase was prepared by controlled, volume glass crystallisation. The bactericidal effect was demonstrated on fracture surfaces of a mechanically ground sample of crystallized glass.

Acknowledgement

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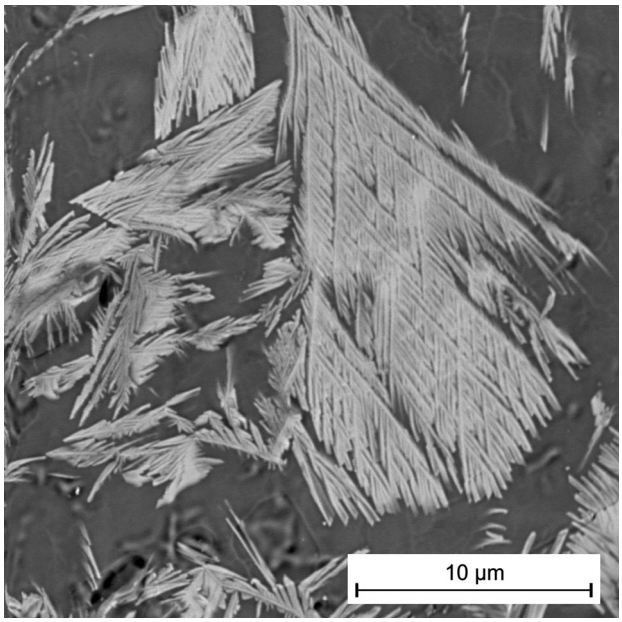

Figure 7. Rutile phase crystals on the glass surface crystallising by heterogeneous nucleation from the platinum surface while the melt is being cooled down (at the temperature of 800°C).

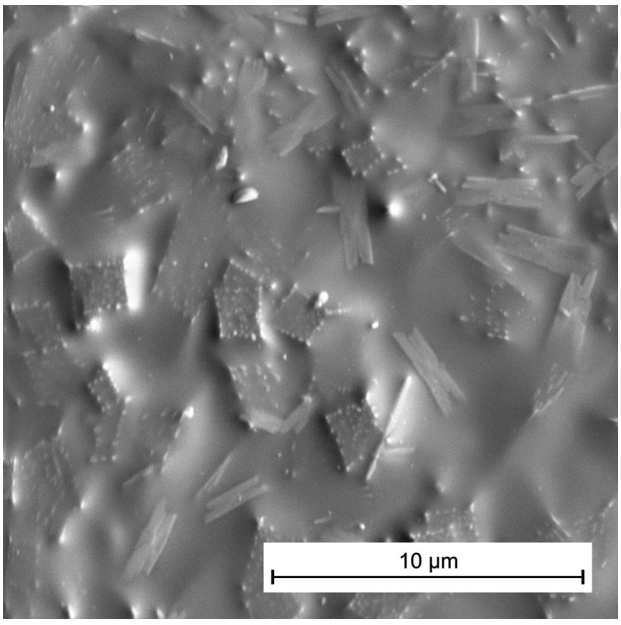

Figure 8. Anatase, rutile and non-identified phase crystals formed on the glass/air boundary while the melt is being cooled down (at the temperature of 750°C).

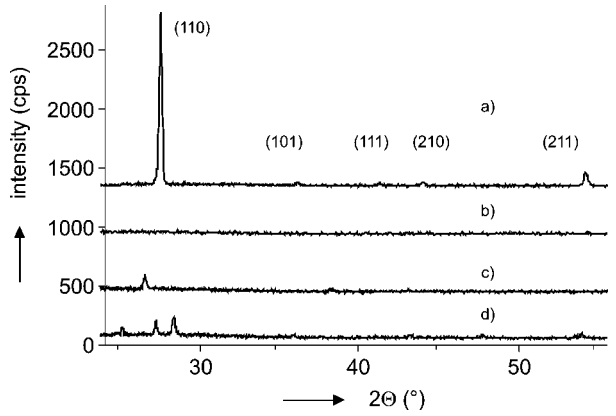

Figure 9. X-ray diffraction analysis (XRD patterns) of sample surfaces - surface-crystallised glass samples prepared by cooling down the melt a) nucleated on the boundary of glass and platinum at the temperature of 800°C and b), c), d) nucleated on the boundary of glass and air at temperatures of 850, 800 and 750°C.

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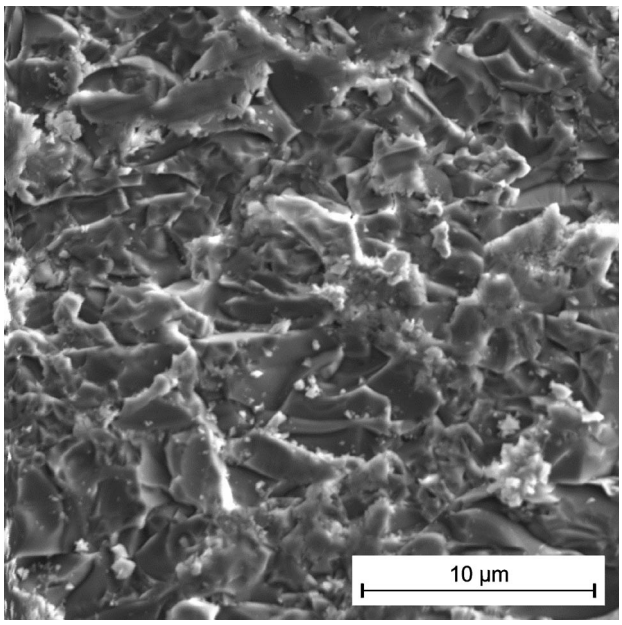

Figure 10. Fracture surfaces of the ground sample (A) of crystallised glass treated by two-step thermal processing.

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ŘÍZENÁ KRYSTALIZACE TiO_2 V ALKALICKOBORITOKŘEMIČITÉM SKLE A JEHO BAKTERICIDNÍ VLASTNOSTI

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Vliv tepelného zpracování na krystalizaci TiO_2 v alkalickoboritokřemičitém skle byl zkoumán diferenciální termickou analýzou, rtg-difrakční analýzou a elektronovou mikroskopií. Povrchy vzorků připravených objemovou a povrchovou krystalizací TiO_2 byly hodnoceny z hlediska baktericidní účinnosti. Řízenou krystalizací skla s nukleací v objemu vzorku byl připraven polykrystalický materiál s jedinou krystalickou fází anatasem s velikostí krystalů 0,01-0,5 mm. Baktericidní účinek byl prokázán na takto připravených vzorcích na lomových plochách mechanicky obroušeného povrchu.