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Ceramics International 35 (2009) 1693–1697

CERAMICS INTERNATIONAL

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Short communication

Novel porous TiO_2 glass-ceramics with highly photocatalytic ability

Tetsuo Yazawa *, Fumiko Machida, Kaori Oki,
Atsushi Mineshige, Masafumi Kobune

Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji-City, Hyogo 671-2201, Japan

Received 24 June 2008; received in revised form 15 July 2008; accepted 14 September 2008
Available online 14 October 2008

Abstract

A porous TiO_2 glass-ceramics with high photo-oxidative activity was successfully obtained from the SiO_2–Al_2O_3–B_2O_3–CaO–TiO_2 glass system. Rutile-type TiO_2 was observed in the crystallization temperature range of 973–1173 K. The band gap of the glass-ceramics coincided approximately with that of rutile-type TiO_2. The photocatalytic activity of this glass-ceramics was about four times larger than that of a TiO_2-coated photocatalyst fabricated by the sol–gel process. Furthermore, as this porous TiO_2 glass-ceramics contained TiO_2 in composition form, it could prevent peeling of the TiO_2 from the substrate. As well, this glass-ceramics can be easily shaped into sheets, tubes, rods, etc.

Keywords: C. Chemical properties; D. Glass-ceramics; D. Silicate; D. TiO_2

1. Introduction

Photocatalyst such as TiO_2 is widely used in various products such as air purifiers, deodorants, and for sterilization and anti-fouling [1]. However, the photocatalysts are used in dispersed form and are very difficult to collect after use. To overcome this shortcoming, photocatalysts have recently been developed in which TiO_2 was coated on appropriate substrates, such as a ceramic, glass or metal plate, or glass tube, by the sol–gel process [2–5]. However, in these applications, the coated TiO_2 easily peels off from the substrate.

One of significant characteristics of glass-ceramics is the excellent formability [6]. In the present study, a novel porous TiO_2 glass-ceramics with highly photocatalytic ability was prepared in the SiO_2–Al_2O_3–B_2O_3–CaO–TiO_2 glass system by the crystallized glass process. As this porous TiO_2 glass-ceramics contains TiO_2 in composition form, it prevents peeling of the TiO_2 from the substrate. And further, this glass-ceramics can be easily shaped into sheets, tubes, rods, etc. Consequently, this glass-ceramics is highly suitable for incorporation into a photocatalytic reactor.

2. Experimental

2.1. Glass melting

The glass was prepared by mixing the desired amounts of the analytical-grade reagents TiO_2, $CaCO_3$, $Al(OH)_3$, SiO_2, $MgHPO_4$, H_3BO_3, ZrO_2 and $Mg(NO_3)_2$. 50 g of the powdered mixture was melted at 1773 K for 3 h in a platinum crucible in an electric furnace, and then cast on a carbon plate.

2.2. Crystallization and acid leaching

Crystallization was performed in the temperature range of 773–1173 K over a period of 15 h. A porous TiO_2 glass-ceramics was obtained by acid leaching with an aqueous solution of 3-N HNO_3 at 371 K for the desired time [7,8].

2.3. Characterization of the glass

Crystals in the glass were analyzed by X-ray diffraction (XRD) measurement with Cu Kα radiation (Mini Flex Rigaku Co.). The TiO_2 content was analyzed by X-ray fluorescence analysis (SEA2001 Seiko Instruments Inc.). The measurement of pore characteristics was performed by N_2 adsorption method

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* Corresponding author. Tel.: +81 79 267 4896; fax: +81 79 267 4896.
E-mail address: yazawa@eng.u-hyogo.ac.jp (T. Yazawa).

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doi:10.1016/j.ceramint.2008.09.011

Table 1
Composition of initial glasses.

	A	B	C	D	E	F
TiO_2	18	20	26	22	20	20
SiO_2	36	29	26	32	25	29
Al_2O_3	12	13	10	13	13	13
CaO	25	28	28	27	28	28
MgO	4	5	5	1.5	9	5
P_2O_5	2	2		3.5		
B_2O_3	2	2	5		5	2
ZrO_2	1	1		1		1
Na_2O						2

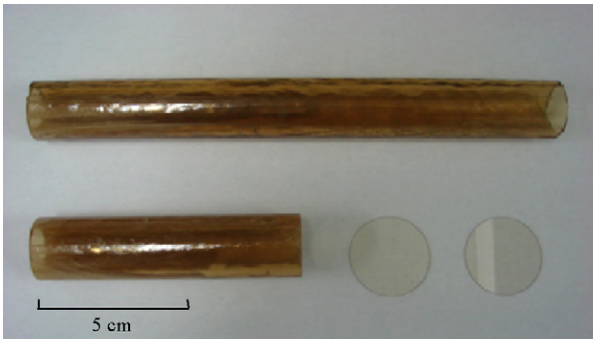


Fig. 1. Photograph of glass shaped into a tube and disk.

(BELSORP-mini BELL JAPAN INC.). The diffusive reflectance spectra were determined by using a photometer (V-650 JASCO Co.) equipped with an integrating sphere accessory.

2.4. Evaluation of photocatalytic activity

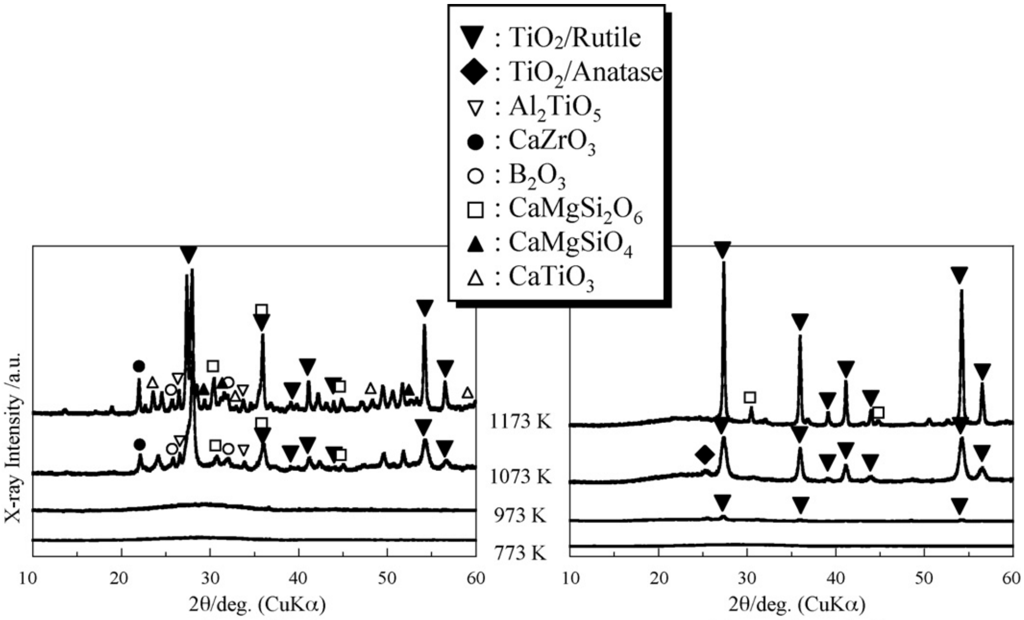
Photocatalytic activity was evaluated by measuring the photo-degradation of a 200 mdm^3 aqueous methylene blue solution with an initial concentration of 56 $\mu mol/dm^3$ [9,10]. A quartz cell was used as the reaction vessel under the irradiation of a 10-W low-pressure mercury lamp (Model UVL10DL-12, Sen Tokusyu Kogen Ltd.). The weight of the glass-ceramics used in each measurement was 1.0 g. The concentration of methylene blue was determined by a spectrophotometer (U-1100 HITACHI Co.) at 664 nm.

To avoid the influence of adsorption on the porous glass-ceramics surface, the samples were soaked in an aqueous methylene blue solution with the same concentration for 24 h under a reduced pressure of 0.1 abs. MPa in order to attain adsorption equilibrium prior to photocatalytic activity measurement. To attain adsorption equilibrium rapidly, the samples were acid leached for 15 min in order to obtain a thin porous layer on the sample surface.

3. Results and discussion

3.1. Glass

Table 1 tabulates the compositions of the initial glasses used. Composition F was the best glass-forming, consequently the best formability judging from its transparency and XRD measurement. This may be attributed to the addition effect of Na_2O. The second and third were A and B, respectively. A and B were slightly brownish, clear glasses. After crystallization, F showed no TiO_2 crystal peak, as revealed by XRD, while A showed a very clear TiO_2 peak, as described in Section 3.2. The addition of Na_2O might play some role on the inhibition of TiO_2 crystallization by decreasing glass transition temperature [11]. The larger the content of TiO_2 crystals in glass-ceramics, the larger the photocatalytic activity. In this meaning, C is expected of high photocatalytic activity. However, the larger the content of TiO_2 in glass-ceramics, the smaller the formability by its



Crystallized

After acid reached

Fig. 2. XRD patterns of the glass-ceramics for various crystallization temperatures.

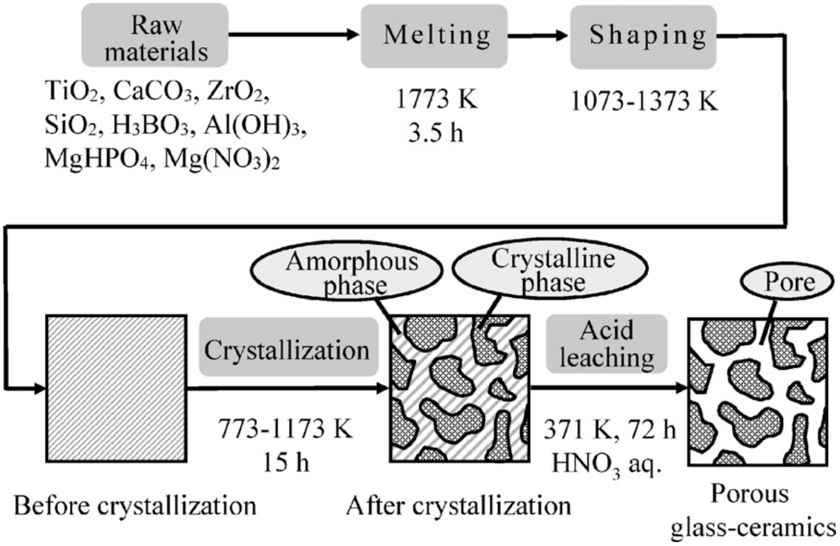


Fig. 3. Preparation process of the porous glass-ceramics.

crystallization of TiO_2. Hence, in the present paper, composition A was used. Fig. 1 shows a photograph of glass A shaped into a tube and a disk.

3.2. Crystallization and acid leaching

Crystallization was performed in the temperature range from 773 to 1173 K over 15 h. Fig. 2 shows XRD patterns of glass samples for various crystallization temperatures. Rutile-type TiO_2 was observed in the crystallization temperature range of 973–1173 K. The crystal size was 25 nm under 1173 K for 15 h on the basis of the Sherrer's formula [12]. Crystallization was followed by acid leaching in order to obtain a porous glass-ceramics. As shown in Fig. 2, after a 72-h acid leach, the amorphous halo around 30° disappears. This means the amorphous phase was leached out by the acid leach, and a porous glass-ceramics could be obtained through the process illustrated in Fig. 3. After the acid leach, the amount of TiO_2 was 31 wt.% at a crystallization temperature of 1173 K, while the amount of TiO_2 in the initial glass was 14 wt.%. This result also supports the above process.

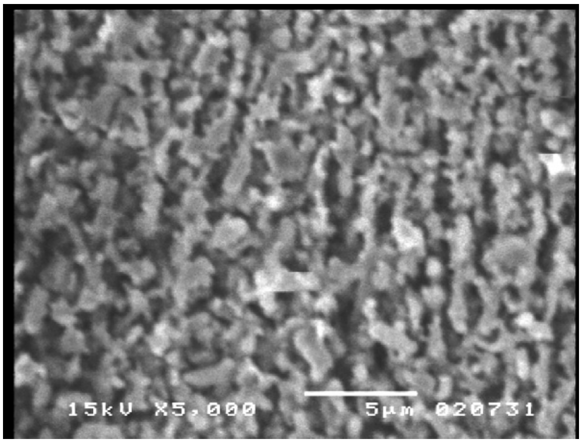


Fig. 4. SEM photo of the glass-ceramics crystallized at 1173 K after acid etching.

Generally, glass-ceramics is broken after acid leaching into small crystalline particles, however, this glass-ceramics can maintain monolith after acid leaching. This may be due to crystallization in the phase structure of interconnected spinodal decomposition as shown in Figs. 3 and 4 shows SEM photo of the glass-ceramics crystallized at 1173 K after acid etching. This photo indicates the interconnected structure characteristic of spinodal decomposition.

Fig. 5 shows diffuse reflectance spectra. The band gap of the present glass-ceramics was about 3.1 eV, which coincides approximately with the band gap of rutile-type TiO_2 [13]. This agrees with the XRD results described above. Fig. 6 is a photograph of the glass-ceramics after crystallization, showing

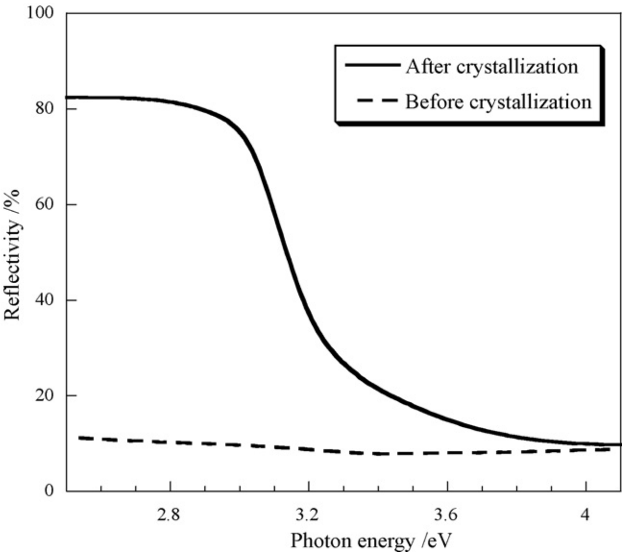


Fig. 5. Diffuse reflectance spectra for before and after crystallization under 1173 K for 15 h.

Fig. 6. Photograph of the glass-ceramics after crystallization under 1173 K for 15 h.

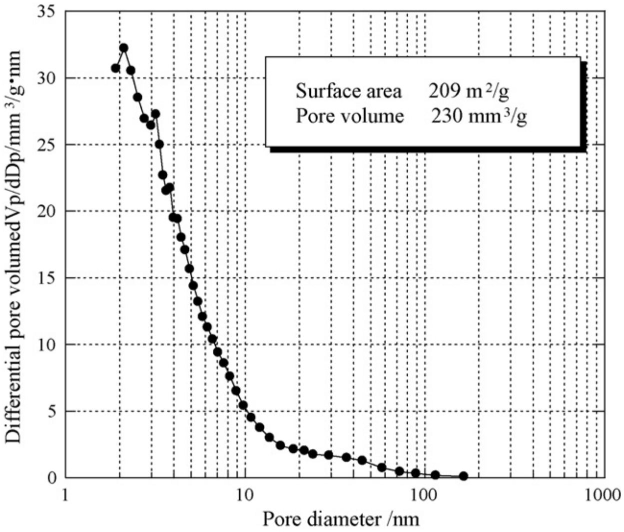


Fig. 7. Pore size distribution of the porous glass-ceramics.

that the glass-ceramics is opaque after crystallization and that crystallization has occurred uniformly in the glass bulk.

3.3. Pore characteristics

Fig. 7 shows the pore size distribution of the glass-ceramics obtained at the crystallization temperature of 1173 K for 15 h after a 72-h acid leach based on the DH method [14]. The pore volume and BET surface area are 230 mm^3/g and 209 m^2/g, respectively. The pore diameter of the porous glass-ceramics is ca. 2 nm.

3.4. Photocatalytic activity

Fig. 8 shows the photocatalytic activity of the porous glass-ceramics for S-1, S-2, S-3 and S-4. The crystallization temperatures of S-1, S-2, S-3 and S-4 were 773, 973, 1073 and 1173 K, respectively. The time of crystallization was kept 15 h for all the samples. Among these, S-4 shows the highest decomposition value. The decomposition value decreases in the order S-3 > S-2 > S-1. This is consistent with the peak intensity of TiO_2 in the XRD shown in Fig. 2: the larger the peak intensity of TiO_2 is, the higher the decomposition value is.

Fig. 9 compares the photocatalytic activity per outer surface area between the present glass-ceramics S-4 and TiO_2-coated glass plate prepared from Ti-alkoxide by sol–gel process (Supplied by Photo-Catalytic Materials Inc., Komaki, Japan, SG2A) [15]. The photocatalytic activity of the former was about four times larger. This may be attributable to the large surface area of the glass-ceramics. After a 15-min acid leach, the BET surface area of the glass-ceramics was ca. 0.5 m^2/g.

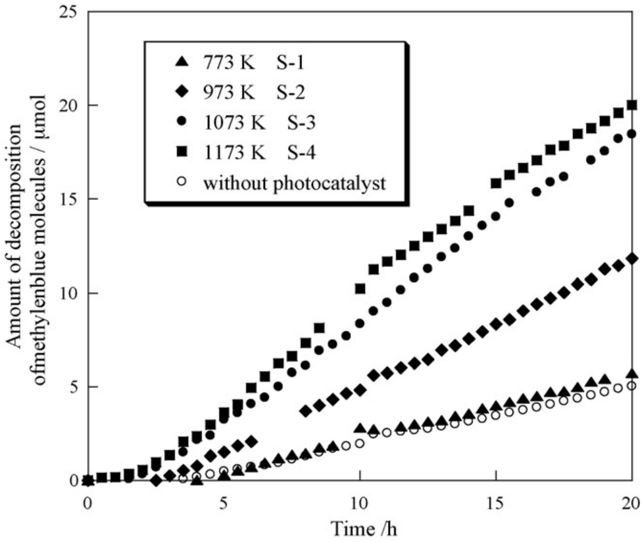


Fig. 8. Photocatalytic activity of the porous glass-ceramics.

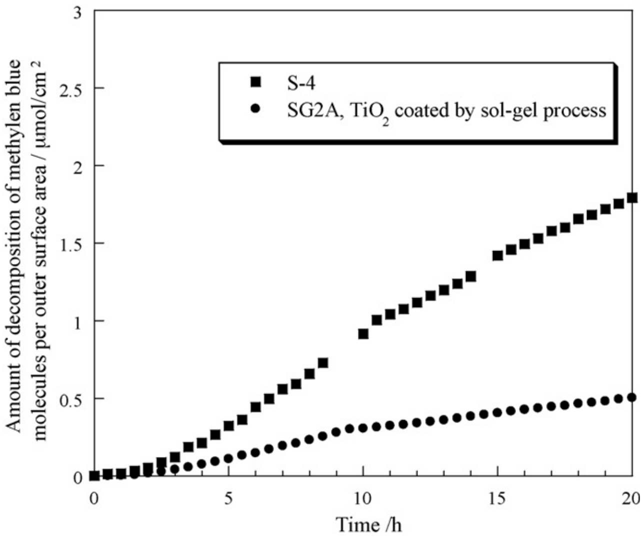


Fig. 9. Comparison of photocatalytic activity between the present porous glass-ceramics (S-4) and the commercially available TiO_2-coated photocatalyst fabricated by sol–gel process (SG2A).

4. Conclusion

A porous TiO_2 glass-ceramics with high photocatalytic activity was successively obtained. The crystal was a rutile-type TiO_2. The band gap of the glass-ceramics coincided approximately with that of rutile-type TiO_2. It also can be easily shaped into sheets, tubes, rods, etc., hence, it is a promising material for devices used in photochemical reactors.

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