The Kinetics of Volatilization of P_2O_5 From Sol-Gel Derved Phosphosilicate Glass-Ceramic Powder

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졸-겔법으로 제조된 Phosphosilicate 유리-요업체 분말로부터의 P_2O_5 휘발 반응 속도론

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ABSTRACT

The kinetics of volatilization of phosphorous oxide from phosphosilicate glassceramic powders prepared by a sol-gel process were investigated at a given temperature. The rate of P_2O_5 vaporization increased with the P_2O_5 concentration in the phosphosilicate powder. Vaporization from the powder containing 46% P_2O_5 was analyzed using a kinetic model for diffusion limited evaporation. The diffusion through phosphosilicate glass in the surface of each particle in the temperature range 800~850℃ are presented.

요 약

졸-겔법에 의해 제조된 Phosphosilicate 유리요업체 분말로부터의 인산화물의 휘발 반응 속도론을 한 온도에서 고찰하였다. P_2O_5의 휘발속도는 Phosphosilicate 분말의 P_2O_5 46%를 함유하고 있는 분말에서의 휘발 반응을 확산에 의해 제어되는 휘발 반응을 위한 반응속도론 모델을 사용하여 분석하였다. 800~850℃의 온도에서 입자의 표면에 존재하는 Phosphosilicate 유리를 통한 P_2O_5의 확산에 대한 확산체수와 활성화에너지를 구하였다.

1. Introduction

Glasses and oxide materials are used in a wide variety of high-temperature applications where volatilization rates and thermodynamic stabilities are often limiting factors. The volatilization causes substantial changes in the properties of the glasses and oxides. The volatilization studies can provide information about diffusion coefficients, reaction rate coefficients and sometimes the component lifetimes.

The kinetics of volatilization from glasses and oxide materials have been studied by many authors[1-5]. Most of these studies have involved the determination of mass loss using a thermobalance. The volatilization products were removed by a flowing gas. From the time dependence of the volatilization loss, one can obtain information regarding the rate controling steps in the volatilization process (surface reaction and/or diffusion control).

The object of this work was the study of the kinetics of volatilization of P_2O_5 from the phosphosilicate glass/ceramic powders. The sol-gel method of making phosphosilicate glass was chosen as a low temperature route since melt forming of these high P_2O_5 content glasses would be difficult due to the high volatility of phosphorus oxide at high temperatures.

The sol-gel process is one of the most promising methods for the manufacture of glass, pure fine pow-

ders and ceramics. The theoretical considerations, processing techniques and applications related to sol-gel derived ceramics have been reviewed by many authors[6-9]. The prime technological importance of the sol-gel process is that it opens up a possibility of preparing homogeneous glasses and glass-ceramics at lower temperatures, which are hard to prepare by melting of oxide mixtures.

Phosphosilicate glasses prepared by the sol-gel method have been studied by a few investigators. Thomas[10] has provided in his patent a method for producing phosphosilicate glasses. Silicon alkoxide was reacted with phosphoric acid to produce a homogeneous gel. By this method granular oxide product consisting of about 8 to about 26 weight percent P_2O_5 and about 92 to about 74 weight percent SiO_2 could be produced.

Jabra et al.[11] has sutdied the gels of the SiO_2-P_2O_5 system prepared by a sol-gel method. Silica was introduced as a hydrosol (LUDOX AS) which is stabilized by the presence of NH_4^+ ions. P_2O_5 was introduced as an aqueous solution of phosphoric acid or ammonium phosphate $(NH_4)_2HPO_4$. Gels containing 5 to 20 mol% of P_2O_5 were prepared and the conversion of gels into glasses was obtained by hot-pressing techniaues using graphite dies.

In this paper we report the preparation and properties of phosphosilicate materials prepared by a sol-gel method.

2. Experimental Procedure

2.1. Preparation of Gels

In this work, phosphosilicate glass-ceramics containing 41 and 46 mol% of P_2O_5 prepared by a sol-gel process were investigated. Phosphosilicate glass-ceramic powders were prepared using tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) and phosphoric acid (H_3PO_4) as raw materials. The general procedure for the preparation of phosphosilicate powders containing 41 and 46 mol% of P_2O_5 is as follows. In a beaker, equal volumes of TEOS and ethanol were mixed together. Phosphoric acid was added slowly into this solution while stirring with a magnetic stirring rod. The mixed solution was covered with aluminum foil and stirred at ~45℃ on a hot magnetic stirring plate. But, due to the high concentration of P_2O_5, the gelation proceeded rapidly in

one to two hours. Dried gels were opaque with a large concentration of small pores, and it was very difficult to remove organics from these gels by heat treatment. So, phosphoric acid was mixed with about 18 moles of water per mole of phosphoric acid before adding it to TEOS. The gelation proceeded more slowly and glassy gels were obtained. These phosphosilicate gels were dried at 45℃ in an oven.

All the gels after drying at ~45℃ were hand-ground with a mortar and pestle. The powders were heated to 500℃ at a rate of 0.5℃/min. in flowing oxygen and held for 4 hours at 500℃. These phosphosilicate gel powders heat treated at 500℃ were sieved to −200 mesh for further analysis.

2.2. Measurements of Properties

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to determine the physical and chemical reactions and the weight loss characteristics of the powders during heating.

Thermogravimetric analysis was performed on powders to study the volatilization kinetics at various temperatures. An automated thermal analyzer was used for all samples at temperatures up to 1000℃. The flow rate of the carrier gas, oxygen, was maintained at 0.2 SLPM during TGA.

Differential thermal analysis was carried out on powders to observe any reactions occurring in the gels during heating. All data were obtained using an automatic recording analyzer with a 1600℃ DTA cell. Prior to performing the DTA, the module was calibrated against the melting point of gold Alpha-alumina was used as the reference material for DTA. About 30 mg of powder was packed into a platinum cup sample holder and analyzed at a heating rate of 10℃ per minute with compressed air flowing at 0.2 SLPM.

Identification of crystalline phases in the glass-ceramic powder samples was obtained by an automated X-ray diffractometer. A CuK-α source was used for all analyses. The pattern were generally run at 1° 2θ per minute. The powders were ground with a mortar and pestle and passed through a 200 mesh sieve before insertion into the sample holder.

The microstructures of the phosphosilicate glass-ceramic powders were observed by transmission electron microscopy (TEM). The powder to be analyzed
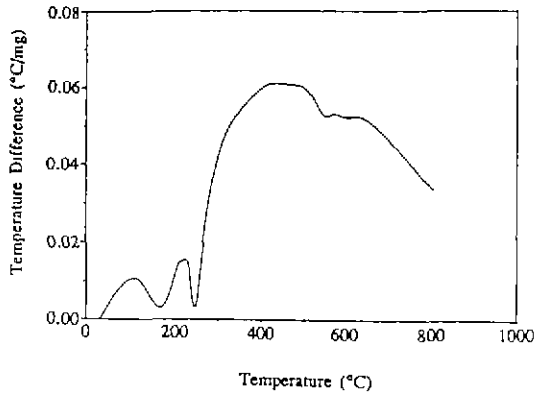
Fig. 1. Differential thermal analysis of the 46% phosphosilicate gel dried at 100℃.
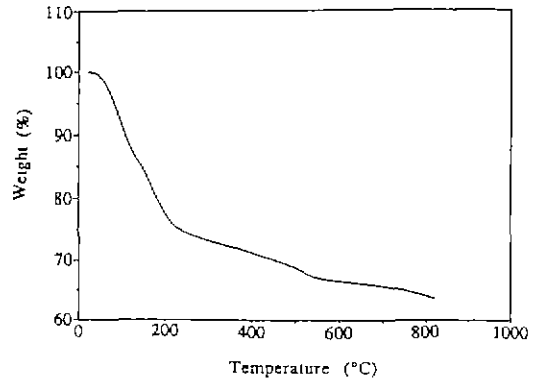

Fig. 2. Thermogravimetric analysis of the 46% phosphosilicate gel dried at 50℃.

was dispersed in methanol and a drop of the slurry was placed on a carbon coated copper grid. The TEM was operated at an accelerating voltage of 120 kV for all samples.

3. Resusts and Discussion

3.1. Thermal Analysis

DTA of the phosphosilicate gel with 46 mol% of P_2O_5 dried at 100℃ was carried out at a heating rate of 5℃ per minute in flowing oxygen. The DTA curve is presented in Fig. 1. Two endothermic peaks were observed at ~160° and ~250℃. The endothermic peak at ~160℃ is attributed to the physical desorption of water and the solvents trapped inside the gel. The other endothermic peak observed at ~250 is suspected to be due to the evaporation of the water dissociated from the phosphoric acid. It was reported that water is dissociated from phosphoric acid at ~213℃[12].

From the TGA analyses little weight loss was observed at temperatures of 700 to 900℃ for the gels of which the phosphorus concentrations were less than 40 mol%. The TGA curve of the 46 mol% gel, run at a heating rate of 5℃ per minute in flowing oxygen, is presented in Fig. 2. A large weight loss was observed at temperatures below 250℃, which supports the explanation of the peaks shown in the DTA curve. The slow weight loss at temperatures above 250℃ was suspected to be due to the further desorption and oxidation of the organic residues.
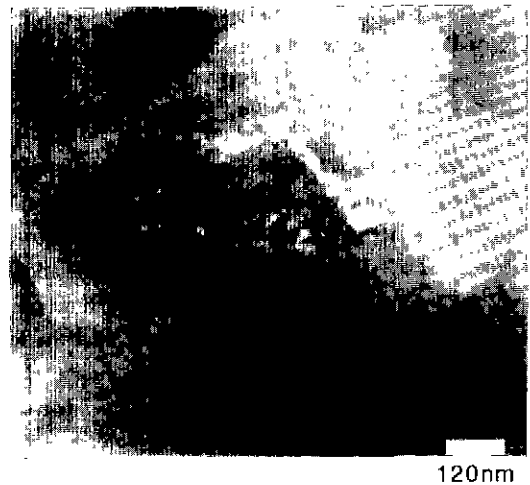
3.2. Microstructure

Fig. 3. TEM dark field image of the 46% phosphosilicate glass-ceramic powder heat treated at 800℃.

The microstructures of the phosphosilicate glass-ceramic powder with 46 mol% of P_2O_5 were examined by transmission electron microscopy (TEM). A TEM micrograph of the powder is shown in Fig 3. The crystalline phase, which was identified as $Si_3(PO_4)_4$ by X-ray diffraction analysis, is surrounded by the glass phase. It is suspected that P_2O_5 is evaporated from the surface of the glass phase. As P_2O_5 is depleted from the surface of each particle, the evaporation of P_2O_5 from the glass-ceramic powders may be controlled by P_2O_5 diffusion through a depleted layer, by the desorption reaction or by gas phase diffusition.
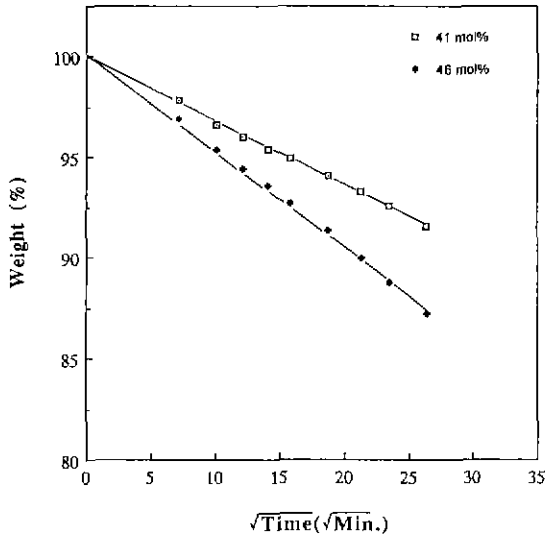
3.3. Kinetics of Volatilization

Fig. 4. Percentage weight remaining of 41 and 46% phosphosilicate glass-ceramic powders at 850℃ as a function of square root of time.

Fig. 5. Percentage weight loss of the 46% phosphosilicate glass-ceramic powder as a function of square root of time.

The kinetics of volatilization of P_2O_5 from the glass-ceramic powders has been studied using TGA. Isothermal TGA was carried out on the powders in flowing nitrogen. The percentage weight loss of 41 and 46 mol% powders at 850℃ is presented as a function of square root of time in Fig. 4. It is shown that the loss rate at 850℃ increased as the concentration of P_2O_5 in the powder increased. The linear dependence of the weight loss on the square root of time, as shown in Fig. 4, indicates that the volatilization of P_2O_5 from both powders at 850℃ is a diffusion controlled process.

For a diffusion controlled volatilization process, a simple graphical method has been developed for determining the diffusivity from weight loss with the solution[3]:

$$Q = C_0 \sqrt{\frac{D}{\pi}} \sqrt{t} \qquad (1)$$

where; Q = the quantity of material lost per unit surface area after time t

Co = initial concentration at the surface

D = the diffusion constant(cm²/unit time)

The above equation can be rewritten for the ddiffusion constant as:

$$D = (\frac{Q}{\sqrt{t}})^2 \frac{\pi}{C_0^2} \qquad (2)$$

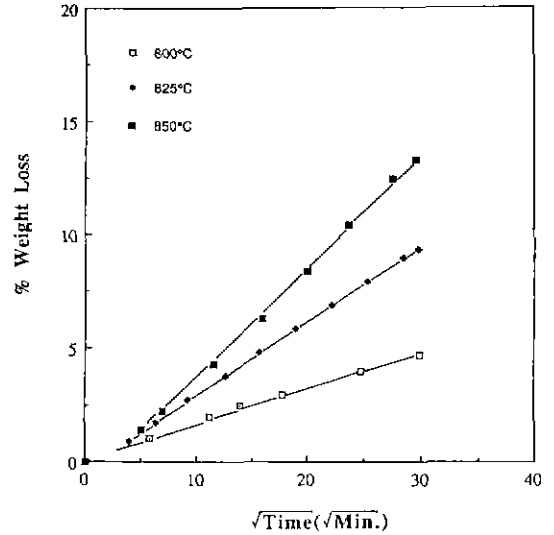If the initial concentration is known, an estimate of the value D may be obtained from the graphical plot which provides a value for the slope $(Q/\sqrt{t})$ The activation energy, E, for the diffusion process can be obtained from the diffusion coefficients for various temperatures by the relationship:

$$D = D_0 \exp(-\frac{E}{RT}) \qquad (3)$$

where R is the gas constant and T is the absolute temperature.

The diffusion coefficients for P_2O_5 diffusion through the phosphosilicate glass at 800, 825 and 850℃, were estimated from the parabolic weight loss curves of 46 mol% glass-ceramic powders, which are presented in Fig. 5. The slopes of the curves were determined by regression analysis and the surface area of 46 mol% powder was assumed to be the same as the specific surface area of 56 mol% powder which is about 3.5 m² /g. The specific surface area of 56 mol% glass-ceramic powder was measured by the three point BET method. This analysis assumes that each powder particle acts independently as a source for P_2O_5 and that any gas phase boundary layers are negligible in thickness so that solid state diffusion of P_2O_5 to the surface where evaporation occurs rapidly is the rate controlling step in P_2O_5 volatilization from each particle. The diffusion
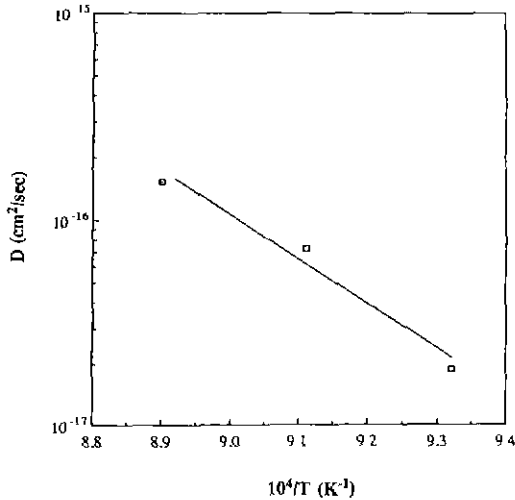
Fig. 6. Arrhenius plot of the diffusion coefficients.

coefficients were calculated using equation (2) to be 1.88×10^{-17}, 7.30×10^{-17}, and $1.53 \times 10^{-16} cm^2/sec$ at 800, 825 and 850℃, respectively. From the Arrhenius plot of the diffusion coefficients (Fig. 6), the apparent activation energy was determined to be ~4.35 eV. Many investigators[14-16] have reported the diffusion coefficients and the activation energies for phosphorus diffusion in silica at higher temperatures (1100℃ and greater). To compare the diffusion coefficients estimated in the present work with those in the literature, the data in Fig. 6. was extrapolated to 1100℃. A value of $5.49 \times 10^{-13} cm^2/sec$ was estimated for the diffusion coefficient at 1100℃. The values reported in the literature are widely scattered from 1.7×10^{-15} to $2.0 \times 10^{-13} cm^2$/sec.

By analyzing each individual particle as a P_2O_5 source where volatilization is rate limited by diffusion of P_2O_5 to the surface, one can estimate the diffusion length for a one hour diffusion at 850℃. The diffusion length, $\sqrt{Dt}$, for 1 hour diffusion at 850℃ was calculated to be ~70Å, which is consistent with the hypothesis that the evaporation of P_2O_5 from 46 mol% glass-ceramic powder is a process rate controlled by P_2O_5 diffusion through a depleted layer in the surface of each particle.

4. Conclusion

The phosphosilicate glass-ceramic powders were prepared by a sol-gel process and their thermal properties and the kinetics of volatilization of P_2O_5 were studied. The following conclusions have resulted from this investigation.

1. The rate of P_2O_5 vaporization from a phosphosilicate powder was sensitive to the composition of the powder. The rate of P_2O_5 vaporization increased as the P_2O_5 concentration in a phosphosilicate powder increased. The rate of loss as a function of time was provided.

2. Vaporization from 46 mol% glass-ceramic powder has been analyzed using a kinetic model for diffusion limited evaporation. The diffusion coefficients for the P_2O_5 diffusion through phosphosilicate glass was estimated from the weight loss curves at 800, 825 and 850℃ to be 1.88×10^{-17}, 7.30×10^{-17} and $1.53 \times 10^{-16} cm^2$/sec at 800, 825 and 850℃, respectively. From the Arrhenius plot of the diffusion coefficients, the apparent activation energy was determined to be ~4.35 eV.

Acknowledgement

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