The Korean Journal of Ceramics, **5**[4] 336-340 (1999)

Properties of Glass-Ceramics in the System CaO-TiO_2-SiO_2 with the Additives of Al_2O_3, ZrO_2 and B_2O_3 for Use in the Solid Oxide Fuel Cells

Jun Suk Lee, Min Jin Park, Hyun Ick Shin and Jae Chun Lee

Department of Inorganic Materials Engineering, Myongji University, San 38-2, Namdong, Youngin, Kyunggido, Korea 449-728

(Received September 28, 1999)

Glasses in the system CaO-TiO_2-SiO_2-Al_2O_3-ZrO_2-B_2O_3 were investigated to find the glass seal compositions suitable for use in the planar solid oxide fuel cell (SOFC). Glass-ceramics prepared from the glasses by one-stage heat treatment at 1,000°C showed various thermal expansion coefficients (i.e., $8.6\times10^{-6}°C^{-1}$ to $42.7\times10^{-6}°C^{-1}$ in the range 25-1,000°C) due to the viscoelastic response of glass phase. The average values of contact angles between the zirconia substrate and the glass particles heated at 1,000-1,200°C were in the range of 131°±4°~137°±9°, indicating that the glass-ceramic was in partial non-wetting condition with the zirconia substrate. With increasing heat treatment time of glass samples from 0.5 to 24 h at 1,100°C, the DC electrical conductivity of the resultant glass-ceramics decreased from $14\times10^{-5}\ \Omega^{-1}cm^{-1}$ to $4.0\times10^{-5}\ \Omega^{-1}cm^{-1}$ at 800°C. Isothermal hold of the glass sample at 1100°C for 48h resulted in diffusion of Ca, Si, and Al ions from glass phase into the zirconia substrate through the glass/zirconia bonding interface. Glass phase and diffusion of the moving ion such as Ca^{2+} in glass phase is responsible for the electrical conduction in the glass-ceramics.

Key words: Glass-ceramics, Zirconia solid oxide fuel cell, Contact angle, Electrical conductivity, Glass seal

I. Introduction

Solid oxide fuel cells (SOFC's) convert the chemical energy of a fuel such as hydrogen into electricity by electrochemical oxidation of the fuel at 800~1,000°C[1]. Fuel cells consist of three electrochemically active ceramics: A porous cathode, a dense yttria-stabilized zirconia (YSZ) electrolyte and a porous anode. In building SOFC's, cells are stacked basically in series and separated from one another by fuel and oxidant flows and bipolar plates such as lanthanum chromite. In planar SOFC's, gas-tight seals operative at the cell operating temperature are required along the edges of each cell and between the fuel cell stack and the gas manifolds.

Glass and glass-ceramic materials have been developed for sealing planar SOFC's. Many of them are based on borosilicates[2,3,4]. Their softening temperatures are usually lower than the operating temperatures of the SOFC, i.e., 800-1,000°C. Their role to achieve a gas-tight seal among SOFC composites is reported to be satisfactory except that the glass phase reacts with yttria-stabilized zirconia(YSZ) and lanthanum chromite bipolar plate during operation[5]. Therefore, more rigid glass ceramics in CaO-Al_2O_3-SiO_2 system have been proposed to avoid a possible reaction of the glass phase in the glass ceramics with YSZ electrolyte[6]. It was claimed that due to the bulk crystallization behavior of the glass-ceramic powder solid state sealing could be expected to depress the reaction between the sealant and the SOFC components. However, the reactivity of the glass-ceramics with the YSZ electrolyte was not reported.

Glasses in the CaO-TiO_2-SiO_2 system also have been studied to use them as solder glass in fuel cells[7]. It was claimed that the incorporation of TiO_2 into the glass network enhanced microhardness and toughness, and improved chemical durability as the percentage of TiO_2 increased. Glass with TiO_2 content of 10~30 mol% had high transformation temperatures ranging from 745 to 759°C and softening temperatures ranging from 764 to 801°C.

The present work deals with the preparation and characterization of glasses and glass-ceramics in the CaO-TiO_2-SiO_2 systems with the additives of B_2O_3, ZrO_2 and Al_2O_3 to obtain glass-ceramic sealant of high electrical resistance and thermal expansion coefficient close to that of zirconia electrolyte. The wetting characteristics of glasses play an important role in a variety of sealing processes. However, in the literature, particularly regarding glass sealant for SOFC's, it is not common to describe the wetting properties of sealing glasses. In this work, we have attempted to measure contact angles between the fused glass sealant and the zirconia electrolyte substrate. Contact angle larger than 90 degree may be desirable for sealing glass because it may help to prevent the spreading of glass melts into the stack components. While the effects of glass compositions and heat-treatment conditions on the various properties of glass ceramics have been studied extensively, little work has been done to find the effects of such parameters on the high tem-

Table 1. Glass compositions (wt%)

Glasses	CaO	TiO_2	SiO_2	Al_2O_3	ZrO_3	B_2O_3
G1	27.7	19.8	29.7	4.6	5.5	12.7
G2	27.3	19.5	29.2	9.1	5.5	9.4
G3	27.0	19.3	29.0	4.5	10.9	9.3
G4	30.3	21.7	32.5	3.1	3.8	8.6

perature electrical conductivity. In this paper, we report the high temperature DC electrical conductivity of glass ceramics produced with different heat-treatment periods.

II. Experimental Procedure

2.1. Preparation and characterization of glasses

Glass samples of the compositions shown in Table 1 were prepared using reagent grade powders. The raw materials ground with alumina mortar and pestle were melted in a platinum-rhodium crucibles at 1,450°C for two hours. The glass melt was quenched on a stainless steel plate and the glass obtained was melted again to prepare homogeneous glasses. Differential thermal analysis of the glass powders(−63+45 μm) were carried out at a heating rate of 10°C/min up to 1,000°C (DTA 2000, MAC Science). Glass bars for thermal expansion measurements were obtained by quenching glass melts and annealed at 700°C. Thermal expansion measurements of glass samples(4 mm×5 mm×10 mm) were made under a load of 30cN at a heating rate of 10°C/min up to 740°C (Netzsch, DIL 402C).

2.2. Preparation and characterization of glass-ceramics

Glass-ceramics for thermal expansion measurements were prepared by a single heat treatment of the glass bars at 1,000°C for 24 h. Crystalline phases of the glass- ceramics obtained by heating the glasses at 1,000 and 1,100°C for 2, 12 and 24 h were identified by powder X-ray diffraction using CuKα radiation (Shimadzu, XD-D1).

Contact angles of molten glasses on TZ8Y zirconia substrate were measured at room temperature using an optical microscope. Four pieces of glasses of about 1mm in size were placed on a strip of TZ8Y zirconia substrate. They were heated to a predetermined temperature, i.e., 1,000, 1,100 and 1,200°C at a rate of 5°C/min, maintained at the temperature for 2 h and cooled down to ambient temperature inside the furnace. The zirconia strip wetted by molten glasses was mounted in resin and polished for observation of the contact angles. Interaction of molten glass and zirconia substrate was investigated with an electron probe micro analyzer (Jeol, JXA 8600).

Glass-ceramics for high temperature DC electrical conductivity measurements were prepared by a single heat treatment of the glass bars at 1,000°C for 0.5, 2, 12 and 24 h. Rectangular shaped sample (6 mm×6 mm×2 mm) was cut from the glass-ceramics. The faces of the samples were polished and gold electrodes were coated on opposite faces. Two-point DC conductivity measurements were carried out using a digital multimeter (HP 34401A) for the samples maintained at 600, 700 and 800°C, respectively.

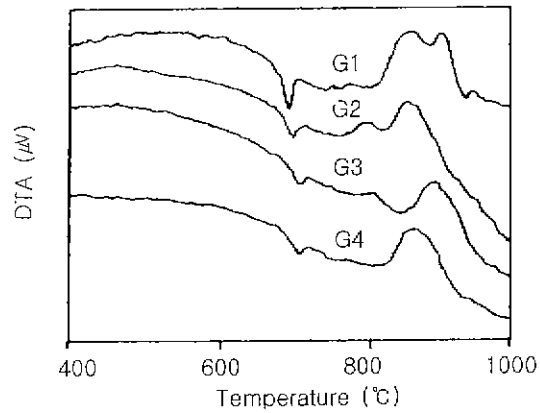

Fig. 1. DTA thermograms of glasses.

Table 2. DTA analysis of glasses

Glasses	Glass Transition Tg (°C)	Endothermic Peak (°C)	Crystallization Temperature (°C)	
			Tx_1	Tx_2
G1	660	700	855	905
G2	670	705	805	865
G3	680	715	815	900
G4	680	715	875	-

III. Results and Discussion

The DTA results for the glasses in Table 1 are given in Fig. 1 and Table 2. The glass transition temperatures estimated by DTA of glasses are in the range of 660~680°C. Boric oxide has a relatively low melting point of 460°C and itself is a network forming ion to form a glass. Since network forming ions increase the electrical conductivity of glass much less than do the network modifying ions, such as alkali and alkali earth element, B_2O_3 in this study have been used to lower melting point of glass without increasing the electrical conductivity. Zirconium dioxide effective as a nucleating agent is the most refractory material among the glass compositions shown in Table 1. Glass G3 which contains relatively higher amount of ZrO_2 shows the highest glass transition temperature of 715°C. Glass G1 which contains relatively higher amount of B_2O_3 shows the lowest glass transition temperature of 660°C. For glasses G1, G2 and G3, two exothermic peaks are observed at 805~905°C. On the other hand, glasses G4 exhibits only one exothermic peak at 875°C. These peaks are attributed to the crystallization of m-ZrO_2 at 755~805°C and ZrO_2 derivatives at 895~955°C[7].

Thermal expansion behavior and thermal expansion coefficients of glasses are shown in Fig. 2 and Table 3, respectively. The glass transition temperatures (Tg's) estimated by dilatometer are in the range of 670~690°C, which is 10~20°C higher than those by DTA. Glasses in the CaO (26~42 wt%), TiO_2 (13~37 wt%), SiO_2 (28~62 wt%) ternary

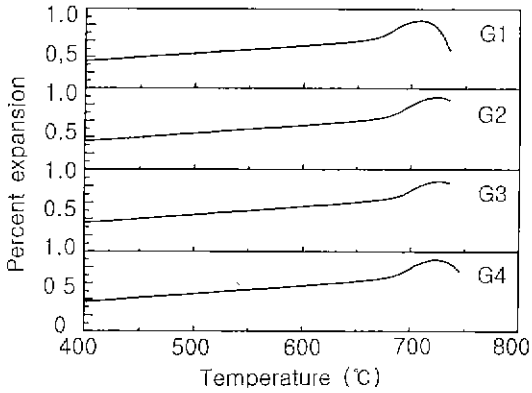

Fig. 2. Thermal expansion curves of glasses.

Table 3. Thermal Expansion Coefficients (α, 400-600°C), Glass Transition Temperatures (Tg) and Softening Temperatures (Ts) of Glasses

Glasses	$\alpha_{400\text{-}600°C}$ ($\times10^{-6}°C^{-1}$)	Tg (°C)	Ts (°C)
G1	9.6	670	710
G2	9.7	680	725
G3	9.8	690	725
G4	10.0	685	725

system are known to have Tg estimated by dilatometer in the range 745~759°C[6], which is 70°C higher than glasses prepared in this study. As expected, addition of B_2O_3, Al_2O_3 and ZrO_2 lowers the Tg of the ternary glass. In the range of 400~600°C, thermal expansion coefficients vary from 9.6×10^{-6} to 10.0×10^{-6} °C^{-1}. Although the glass transition temperatures estimated by dilatometer are in the range of 670~690°C, the softening temperatures of the sample glasses except the glass G1 are the same, i.e., 725°C.

Fig. 3 shows a plot of thermal expansion versus temperature for the heat-treated glasses at 1,000°C for 24 h. Heat-treated glass samples G1 and G2 show thermal expansion coefficients range from 8.4×10^{-6} to 9.6×10^{-6}°C^{-1} which is comparable to that of zirconia electrolyte, i.e., 10.0~10.6×10^{-6}°C^{-1}. As can be seen from Fig. 3, the measured data can be divided into three regions. In the first region corresponding to temperatures below about 650°C, so called the "glassy state" shows an elastic thermo-mechanical response. The second region corresponds to the higher temperature range, i.e., 680~770°C, where the structure of the glass phase in the glass-ceramics becomes so called the "viscous liquid state", the thermal expansion coefficients vary from 33.6×10^{-6} to 42.7×10^{-6}°C^{-1} which is four or five times those measured from the expansion curves below 650°C as shown in Table 4. It is well known that thermal expansion coefficient of glass increases three to five times when the glass transforms from an elastic state to a viscoelastic state[8]. However, at temperature above 800°C, which corresponds to the third region, measured data for linear expansion of the heat-treated glasses show a large decrease in the thermal expansion coefficent. This thermal expansion behavior is attributed to the stress relaxation of glass phase in the liquid state and to the elastic response of crystalline phase in the heated-treated glass at high temperature.

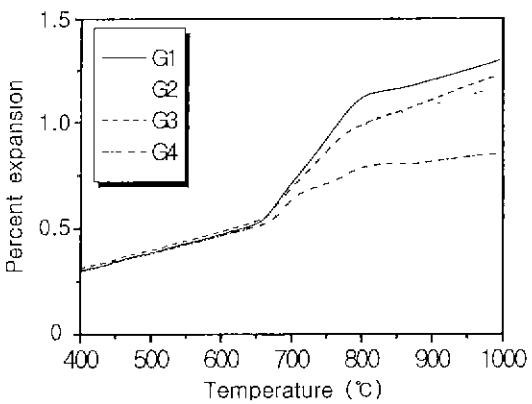

Fig. 3. Thermal expansion curves of the heat-treated glasses at 1,000°C for 24 h.

Table 4. Thermal Expansion Coefficients α ($\times10^{-6}°C^{-1}$), of the Heat-treated Glasses at 1,000°C for 24 h

Heat-treated glasses	$\alpha_{400\text{-}600°C}$ ($\times10^{-6}°C^{-1}$)	$\alpha_{680\text{-}770°C}$	$\alpha_{880\text{-}990°C}$
G1	8.6	42.7	9.6
G2	8.4	33.6	9.4
G3	8.7	34.6	12.9
G4	8 5	–	4.3

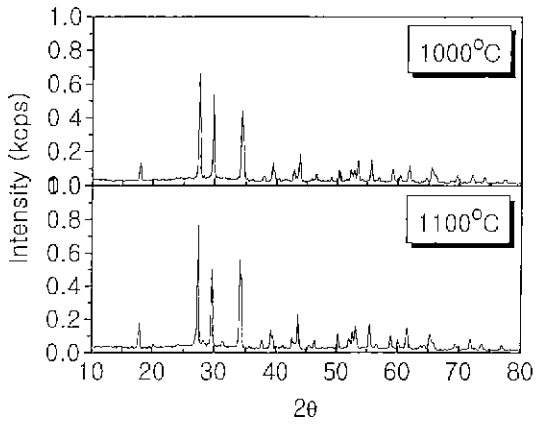

Fig. 4. XRD powder patterns of the heat-treated glass G1 at (a) 1,000°C and (b) 1,100°C for 2 h.

In Fig. 4, XRD powder patterns of the heat-treated glass G1 at 1,000 and 1,100°C for 24h show major peaks at 2θ=27.5°, 29.7°, 34.2°, 43.7° and 53.6°. The peak intensity slightly increases with the heat-treatment temperature of glass. The crystalline phase has been identified as sphene, $CaOTiO_2SiO_2$. Crystalline phases such as $CaAl_2Si_2O_5$, $ZrTiO_4$ and $CaTiO_3$ formed by reaction of TiO_2 and ZrO_2 or CaO and TiO_2 have not been detected[9]. Micrographs of the heat-treated glasses G3 at 1,050 and 1,100°C are shown in Fig. 5. Morphology of crystalline phase of the heat-treated glass G3 at 1,050°C shows fibrous crystallites 20 to 35 μm in length and 2 to 4 μm in thickness. The thickness of the crystalline phase apparently increases with the heat-treat-

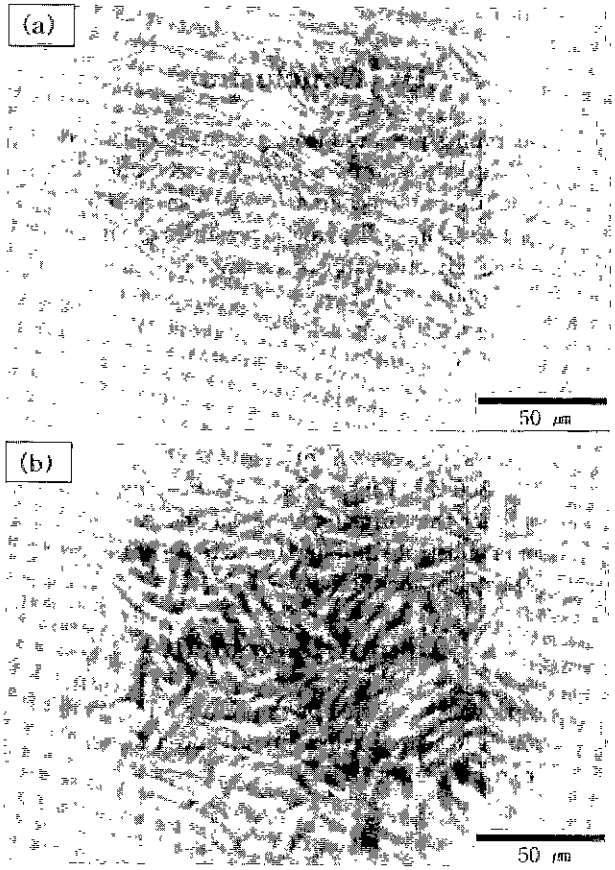

Fig. 5. Micrographs of the heat-treated glasses G3 at (a) 1,050°C and (b) 1,100°C for 2 h.

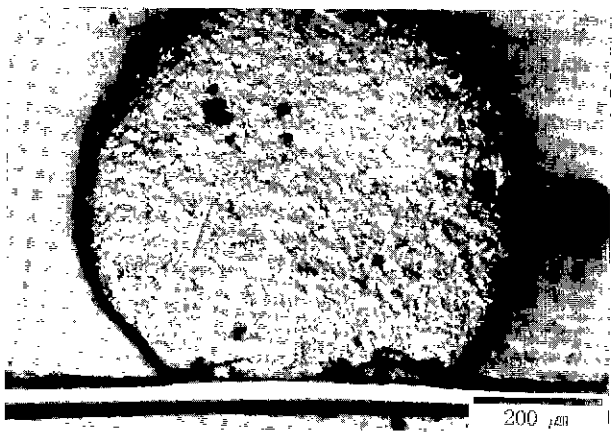

Fig. 6. An optical photograph showing contact angle of 140° for a fused glass-ceramic on zirconia substrate.

ment temperature However, the volume fraction of the crystalline phase does not appear to change noticeably.

Fig. 6 shows an example of the cross-section optical micrograph used for the measurement of contact angle between glass-ceramic particle and zirconia substrate. The wetting response indicates the degree to which the liquid spreads or infiltrates the solid. The averaged value of measured contact angles of the glass G1 heated at 1,000, 1,100 and 1,200°C are 131°±24°, 133°±10° and 137°±9°, respectively.

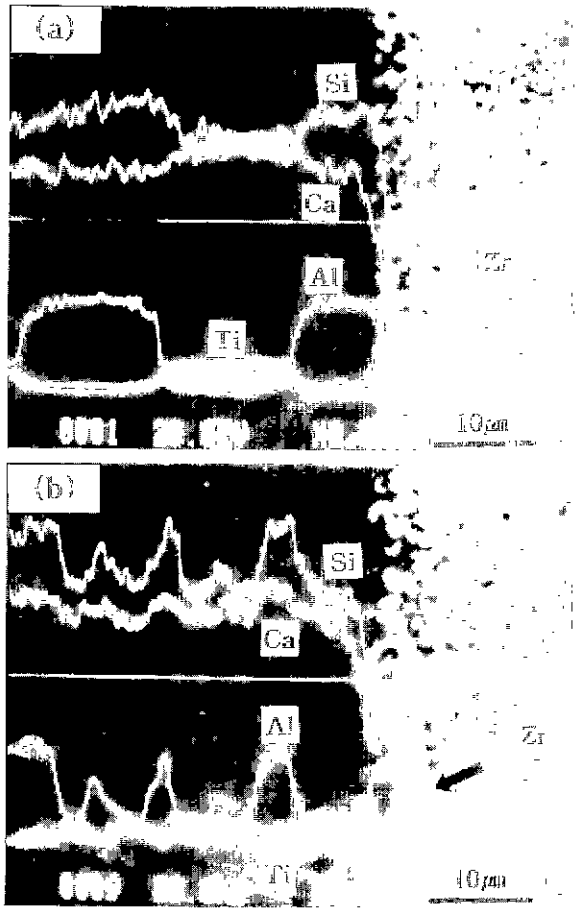

Fig. 7. EPMA elemental line profiles at the interface between glas G1 and TZ8Y zirconia substrate heated at 1,100°C for (a) 24 h and (b) 48 h.

Therefore, we can say that the glass-ceramic particle is in partial non-wetting condition with zirconia substrate. It is generally recognized that a good wetting response implies that an adherent bond is feasible, whereas non-wetting rarely corresponds to an adequate bond. However, the glass phase in the glass-ceramics may allow microscopic wetting and adherence to zirconia substrate Dependence on glass composition and sealing temperature could not be clarified and the reasons for this require further investigation.

Fig. 7 shows the EPMA elemental line scan profiles for selected elements in the interfacial region of glass G1/TZ8Y zirconia substrate heated at 1,100°C for 24 and 48 h, respectively. In a crystalline phase of the glass-ceramic sample, concentration of Ti and Ca elements is relatively high, while glass phase shows higher concentration of Al and Si. The crystalline phase is identified as $CaTiO_3$ previously mentioned. As the heat-treatment time increased from 24 to 48 h, elemental line profiles indicate the diffusion of Si, Ca and Al elements into the grain boundary of zirconia substrate has taken place as shown by an arrow in Fig. 7(b). Unlike these observed for the $CaO-TiO_2-SiO_2-Al_2O_3-ZrO_2-B_2O_3$ glass-ceramic, it had been claimed that the constituents of glass-ceramics in the $ZnO-BaO-SiO_2-Al_2O_3$ system as seal-

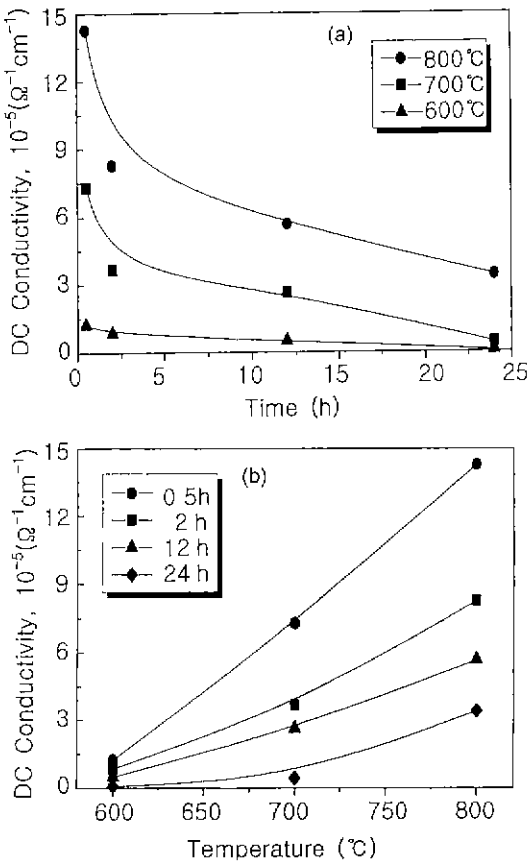

Fig. 8. High temperature DC electrical conductivity of heat-treated glass G1 at 1,100°C as a function of (a) heat-treatment time and (b) measurement temperature.

ing materials, i.e., Zn, Ba, Si and Al, did not diffuse through TZ8Y zirconia substrate after reaction at 1,000°C for 100 h[10]. In the present work, it is assumed that the diffusion of the migrating elements probably occurs through the glass phase rather than the crystalline phase in the glass-ceramic. Reducing the diffusion of the glass forming and the glass modifying ions into the zirconia substrate at high temperature, we need to develop glass compositions as well as heat-treatment schedules to produce glass-ceramics with a less proportion of residual glass.

In Fig. 8, the variation in DC electrical conductivity, σ, for the glass G1 is shown as a function of measurement temperature and heat-treatment time of the samples at 1,100°C. The σ for the glass sample decreases with increasing heat-treatment time. For example, the σ of the heat-treated glass sample measured at 800°C decreases from 1.4×10^{-4} to 4.0×10^{-5} $(\Omega cm)^{-1}$ as the heat-treatment time increases from 0.5 to 24 h. This is attributed to the reduction of glass phase in the heat-treated glass with increasing heat-treatment time, which resulted in the reduction of migrating ions as well as diffusion passage, i.e., glass phase, as mentioned previously. The σ dependence on heat-treatment time is more pronounced with increasing measurement temperature as shown in Fig. 8(b). The similar trend can be found for different heat-treatment temperature of the σ as a function of heat-treatment time.

IV. Conclusions

Glass-ceramics prepared from glasses in the system CaO-TiO_2-SiO_2 with the additives of Al_2O_3, ZrO_2 and B_2O_3 show viscoelastic thermo-mechanical response at 600~1,000°C due to the glass phase. The average values of contact angles between the zirconia substrate and the glass particles heated at 1,000-1,200°C are in the range of 131°±4°~137°± 9°, indicating that the glass-ceramic is in partial non-wetting condition with the zirconia substrate. With increasing heat treatment time of glass samples from 0.5 to 24 h at 1,100°C, the DC electrical conductivity of the resultant glass-ceramics decreases from 1.4×10^{-4} $(\Omega cm)^{-1}$ to 4.0×10^{-5} $(\Omega cm)^{-1}$ at 800°C. Glass phase in the glass-ceramics is responsible for the diffusion of Si, Ca and Al elements into the zirconia substrate and for the increase of high temperature DC electrical conductivity.

Acknowledgements

This work was supported by the Korea Ministry of Education through Research Fund for Advanced Materials made in the program year of 1997.

References

1. Q. Minh, "Ceramic Fuel Cells," *J. Am. Ceram. Soc.*, **76**(3), 568-580 (1993).
2. K. L. Ley, M. Krumpelt, R. Kumar, J. H. Meiser and I. Bloom, "Glass-ceramic sealants for solid oxide fuel cells: Part I. Physical Properties," *J. Mater. Res.*, **11**(6), 1489~1493 (1996).
3. Y. Akiyama, N. Ishida, S. Murakami and T. Saito, US Pat. No. 4, 997, 726 (1991).
4. C. Gunther, G. Hofer and W. Kleinlein, "The stability of the sealing glass AF45 in H_2/H_2O and O_2, N_2 atmospheres," *Electrochemical Proc.*, **97-18**, 746~756 (1997).
5. T. Horita, N. Sakai, T. Kawada, H. Yokokawa and M. Dokiya, "Reaction of SOFC components with sealing materials," *Denki Kagaku*, **61**(7), 760~762 (1993).
6. Y. Sakaki, M. Hatton and Y. Esaki, "Glass-ceramics sealants in CaO-Al_2O_3-SiO_2 system," *Electrochemical Proc.*, **97-18**, 652~660 (1997).
7. H. A. Villegas, A de Pablos and J. M. Fernandez Navarro, "Properties of CaO-TiO_2-SiO_2 Glasses," *Glass Technology*, **35**(6), 276-280 (1994)
8. G. W. Scherer, Relaxation in Glass and Composites, John Wiley & Sons, New York (1986).
9. J. S. Lin and P. Shen, "Fabrication of CaO-ZrO_2-TiO_2-Al_2O_3-B_2O_3-SiO_2 glasses and glass ceramics," *J. Non-Cryst. Solids*, **204**, 135~140 (1996).
10. K. H. Lee, "A study on glasses and glass-ceramics as sealing materials for flat-plate solid oxide fuel cell components," *Kor. J. Ceram.*, **35**(2), 151~162 (1998).