J Mater Sci (2010) 45:3375–3380
DOI 10.1007/s10853-010-4360-4

Fabrication of porous glasses by water vapor corrosion of Y–Al–Si–O–N glass

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Received: 29 June 2009 / Accepted: 27 February 2010 / Published online: 11 March 2010

Abstract The effects of exposure conditions on the microstructural changes of the oxynitride Y–Al–Si–O–N glass system were investigated. The oxynitride glass was exposed to dry O_2 gas, or water vapor containing either O_2 or Ar, at temperatures between 1133 and 1183 K. A porous scale layer was formed by exposure to water vapor, while a non-porous deteriorated scale was obtained only by exposure to dry O_2. Formation of the porous layer was promoted by the presence of oxygen in the water vapor. The corrosion rate of the oxynitride glass in humidified O_2 near the glass transition temperature followed a linear rate law. The morphology of the porous layer was strongly dependent on the exposure temperature, which may be due to the significant decrease in the viscosity of the glass with increasing temperature. The permeability of the porous layer cut from the exposed glass behaved according to Darcy's law; therefore, this layer was considered to be composed of three-dimensional continuous pores. The microstructure of the porous layer could be controlled by the exposure temperature, so that a graded porous glass with different morphological characteristics within the layer could be obtained by exposure to humidified gases at different temperatures.

Introduction

Molten glass coating is an effective technique to prevent the oxidation of carbon materials. The thermal expansion of glass can be made the same as the carbon substrate by adjusting the glass composition, so that the interfacial thermal stress between the substrate and coating glass can be controlled. However, the wettability of carbon to molten glass is very low; therefore, a Si or SiC layer is usually deposited on the carbon as a binding layer prior to glass coating. However, it is well known that Si species derived from the binding layer are oxidized during glass coating, which results in the formation of cristobalite at the carbon–glass interface. The phase transformation of cristobalite, accompanied by large volume shrinkage [1], occurs during the cooling procedure after the coating, which results in crack initiations being induced at the carbon-glass interface. This leads to a significant decrease in the thermal shock resistance of molten glass-coated carbon.

We previously reported carbon substrates completely coated with a silicate glass of the Y–Al–Si–O system, without the production of cristobalite at the carbon–glass interface when the coating was performed at a certain nitrogen partial pressure based on thermodynamic considerations [2]. In addition, it was found that a unique porous glass layer with uniform spherical micro-pores was produced at the glass subsurface when the glass-coated materials were exposed to humidified O_2 near the glass transition temperature of the Y–Al–Si–O glass. The glass-coated carbon with uniform porous glass layer had excellent thermal shock resistance, thermal cyclic fatigue resistance, and steam oxidation resistance. On the other hand, there was no structural change in the glass subsurface when the specimen coated in Ar was exposed to humidified O_2. Therefore, the formation of such a porous glass was considered to be due to the formation of a N_2 dissolution layer at the glass subsurface during coating in N_2, and subsequent water vapor corrosion of the dissolution layer.

The oxidation behavior of the oxynitride Y–Al–Si–O–N glass system in water vapor has been previously investigated

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in detail [3, 4]. Foster et al. [3] reported that the oxidation rate was much faster in water vapor with an O_2 carrier than that with a N_2 carrier, and the oxidation rate followed a linear rate law. Furthermore, it was found that the rate-determining step was controlled by the interfacial reaction between oxide scale and the substrate glass. However, the exposure temperatures were much higher than the glass softening temperature, and therefore the resulting porous oxide scales consisted of large and heterogeneous pores. These porous structures, which are thought to be brittle, are distinct from those obtained in our previous study [2]. On the other hand, it is uncertain whether porous glass with fine and uniform pores can be obtained by the water vapor corrosion of oxynitride glass below the glass softening temperature, in the range that we focus. In addition, the effect of carrier gases on the oxidation behavior of oxynitride glass has not been identified. If the microstructure of porous glass can be controlled by the conditions of water vapor corrosion, the porous materials obtained are expected to be used in filter applications.

The objective of this study is to clarify the effect of the experimental conditions on the microstructural characteristics of porous glass obtained by water vapor corrosion of oxynitride glass. The oxynitride Y–Al–Si–O–N glass system was exposed to wet and dry atmospheres near the glass transition temperature, and the corrosion layers obtained were investigated in detail. The gas permeation properties of the porous glasses were also evaluated to confirm the continuity of pores.

Experimental

The Y–Al–Si–O–N glass was prepared by melting a mixture of oxides and aluminum nitride powders. Y_2O_3 (NR, Daiichi Kigenso Kagaku Kogyo Co. Ltd., Osaka, Japan), Al_2O_3 (AKP-50, Sumitomo Chemical Co., Ltd., Tokyo, Japan), SiO_2 (JIS Guaranteed Reagent, Nacalai Tesque Inc., Kyoto, Japan), and AlN powders (XUS 35560, Dow Chemical Company, Michigan, USA) were used as starting materials. The composition of the AlN powder was 63.1 wt% Al, 32.0 wt% N and 4.9 wt% O, as determined using an oxygen/nitrogen combustion analyzer (EMGA-650, Horiba Ltd., Kyoto, Japan). The initial composition of starting materials was adjusted to 33.1 wt% Y_2O_3, 19.0 wt% Al_2O_3, 46.1 wt% SiO_2, and 1.8 wt% AlN, which corresponds to the $Y_{7.2}Al_{10.2}Si_{18.9}O_{62.6}N_{1.0}$ target composition. The weighed powders were mixed by wet ball-milling in ethanol. The slurry was dried and then passed through a 100 mesh sieve. The resultant powder mixture was set in a carbon mold and melted at 1773 K for 1 h under 1 MPa N_2 in a graphite furnace. The melt was rapidly cooled to 1173 K and annealed at for 10 h, and then cooled slowly to room temperature. The nitrogen content of the Y–Al–Si–O–N glass was examined with an inert gas fusion method using an oxygen/nitrogen combustion analyzer (EMGA-650, Horiba Ltd., Kyoto, Japan). The glass transition temperature (T_g) of the oxynitride glass was determined by dilatometry in a N_2 atmosphere, which was measured with a thermomechanical analyzer (TMA8310, Rigaku Co. Ltd., Tokyo, Japan).

Corrosion experiments were carried out in a quartz glass tube placed in a horizontal electric furnace. Specimens (10 × 10 × 3 mm) were tested at temperatures between 1133 and 1183 K in dry O_2 gas (99.999%) or water vapor containing either O_2 or Ar gas (99.9999%). The volume fraction of the water vapor was adjusted to 80 vol.% using a water pump (PU610, GL Sciences Inc., Tokyo, Japan). The flow rate of the introduced gases was maintained at 1.67×10^{-6} m^3/s, which corresponds to 100 mL/min.

After heat-treatment, cross-sections of the glasses were observed using scanning electron microscopy (SEM; S-4500, Hitachi Ltd., Tokyo, Japan). The distribution of pore size and aspect ratio in the obtained porous layer was determined by image analysis (Scion Image software, Scion Corporation, Maryland, USA) using SEM micrographs. The specimen exposed to dry O_2 gas was analyzed by secondary ion mass spectrometry (SIMS; ADEPT1010, Ulvac-Phi Inc., Japan). The gas permeation properties of the porous glass layer (200 μm thick cut specimen) were determined from the flow rate of N_2 gas under a differential pressure across the porous layer, as measured by a film flow meter (SF-1U, Horiba STEC, Kyoto, Japan).

Results and discussion

The nitrogen content of the prepared Y–Al–Si–O–N glass was 1.1 at%, which was equivalent value to that of the initial composition. The Y–Al–Si–O–N glass had a T_g of 1183 K, which is 20 K higher than that for the nitrogen-free glass (Y–Al–Si–O glass), which has a composition corresponding to $Y_{7.2}Al_{10.2}Si_{18.9}O_{63.8}$ [5].

The effect of exposure to atmospheres on the formation of porous glass was investigated for the Y–Al–Si–O–N glass. Figure 1 shows cross-sectional SEM micrographs of the Y–Al–Si–O–N glass exposed to three different oxidant gases at 1173 K for 100 h. When the glass was exposed to humidified O_2, a porous corrosion layer with a thickness of ca. 65 μm was formed at the glass surface, as shown in Fig. 1a. The specimen exposed to humidified Ar also had a porous corrosion layer, although it was thinner than that obtained in humidified O_2 (Fig. 1b). In contrast, when the glass was exposed to dry O_2 gas, no porous corrosion layer was produced, but a deteriorated scale layer was observed at the surface, as shown in Fig. 1c. From higher

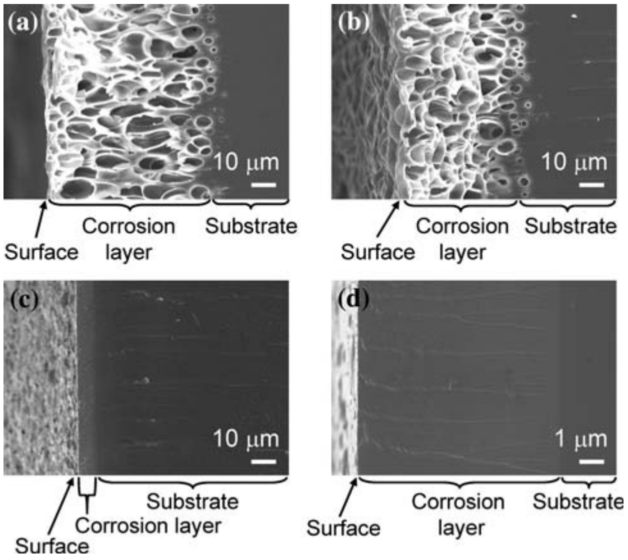

Fig. 1 Scanning electron micrographs of the porous layers formed by exposure of oxynitride glass at 1173 K for 100 h to **a** humidified O_2, **b** humidified Ar, and **c**, **d** dry O_2

magnification SEM image of the glass exposed to dry O_2 (Fig. 1d), the deteriorated scale was approximately 8 μm thickness and obvious structural changes, such as formation of pores or precipitation of crystals, were not observed. These results clarified that water vapor plays an important role in the formation of a porous layer in oxynitride glass. In addition, the presence of O_2 in water vapor accelerates the formation of the porous glass layer. The effects of atmosphere on the formation of porous glass in the oxynitride glass are in good agreement with the oxidation behavior observed in previous research [3].

The specimen exposed to dry O_2 at 1173 K was analyzed by SIMS in order to clarify the compositional change of the deteriorated scale layer. A depth profile of the constituent atoms in the Y–Al–Si–O–N glass with the deteriorated scale layer is presented in Fig. 2. The Y, Al, Si, and O profiles remained constant, regardless of the analysis depth. However, a region of nitrogen depletion was observed at the surface and the thickness approximately corresponded to that of the deteriorated scale layer observed by SEM. Dry O_2 gas at 1173 K oxidizes the oxynitride glass, but it does not induce a drastic structure change, such as observed for the specimen treated in atmospheres containing water vapor. When Si_3N_4 is oxidized under high oxygen partial pressures, it is well known that a SiO_2 film is formed on the surface, which results in the limitation of further oxidation [6]. The oxide layer formed on oxynitride glass is considered to act as an oxidation protective layer in a similar manner as above. The oxidation of oxynitride glass exposed to dry O_2 gas should be controlled by the inward oxygen diffusion through the oxide scale, and therefore the scale growth is expected to be slow.

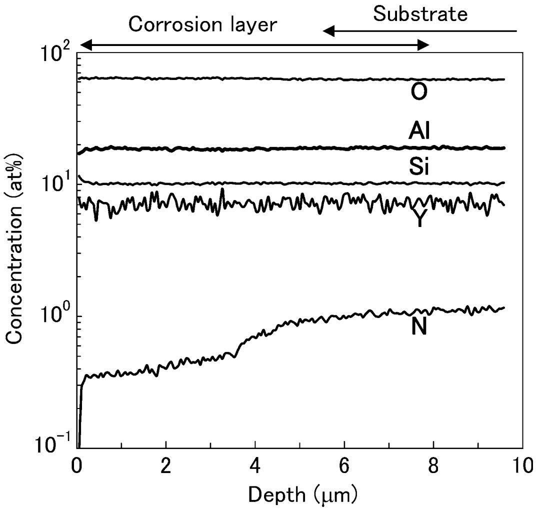

Fig. 2 Depth profile of constituent atoms in the Y–Al–Si–O–N glass exposed to dry O_2 at 1173 K for 100 h, obtained by secondary ion mass spectroscopy

Tulliani et al. [4] suggested that the reaction of oxynitride glass with water vapor could be described by the hydrolysis of Si–N bonds. On the other hand, previous investigations have suggested that water molecules break down the silicon-oxygen network of silicate glasses to form SiOH, and diffusion of oxygen from water occurs through the generation of hydroxyl ions [7, 8]. Such degradation processes of the glass network are considered to be related to the production of the porous layer examined in this study. Si–N bonds are firstly broken by reaction with water, and the generation of N_2 gas is expected to occur. The porous layer can then be produced by evaporation of the N_2 gas with consequent foaming of the glass surface layer. Because the introduction of hydroxyl groups into a silicate glass decreases the viscosity of the glass [9], deformation of the glass is promoted in the presence of water.

Figure 3 shows dependence of exposure temperature and time on the thickness of porous corrosion layer in the Y–Al–Si–O–N glass exposed to humidified O_2. The thickness of porous corrosion layer increased with increase in the exposure temperature. The growth of corrosion layer was proportional to the exposure time; thus the corrosion rate of oxynitride glass observed in this study followed a linear rate law. The rate of porous scale growth in the Y–Al–Si–O–N glass exposed to humidified O_2 at 1163 K was determined to be 0.47 μm/h and the correlation coefficient (*R*) was 0.993. The rate-determining step of water vapor corrosion of the oxynitride glass near the glass transition temperature is considered to be the interfacial reaction between the oxide scale and substrate glass, in a similar manner to that described by Foster et al. [3].

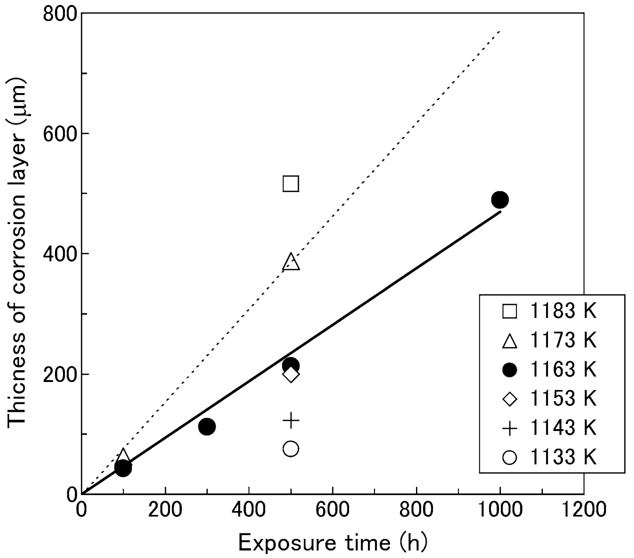

Fig. 3 Dependence of exposure temperature and time on the thickness of corrosion layer in the Y–Al–Si–O–N glass exposed to humidified O_2

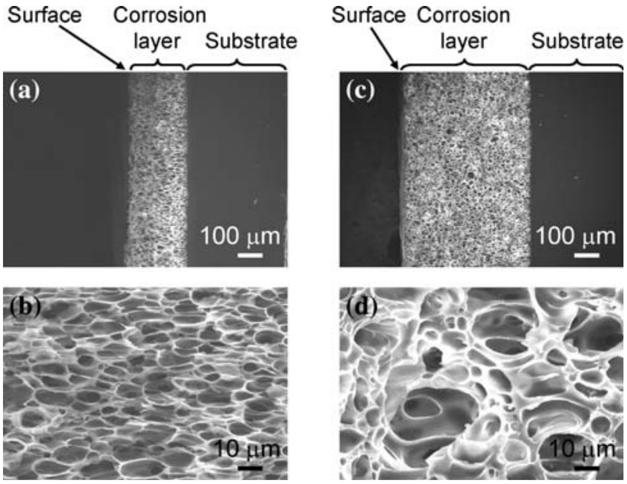

Fig. 4 Cross-sectional SEM micrographs of the Y–Al–Si–O–N glass exposed to humidified O_2 for 500 h at **a**, **b** 1153 K and **c**, **d** 1183 K

Figure 4 shows representative cross-sectional SEM micrographs of the Y–Al–Si–O–N glass exposed to humidified O_2 for 500 h at (a, b) 1153 K, and (c, d) 1183 K. Figures 5 and 6 show the pore size distribution and aspect ratio distribution of pores in the porous layer on the Y–Al–Si–O–N glass exposed to humidified O_2, respectively. The porosity, average pore size, and average aspect ratio of the porous layer are summarized in Table 1. Standard deviations for pore size and aspect ratio of pores are shown in brackets. The microstructure of the porous layer obtained at 1153 K is composed of fine pores and small pore size distribution in comparison to that obtained at 1183 K. On the other hand, the aspect ratio of the pores decreased with increased exposure temperature.

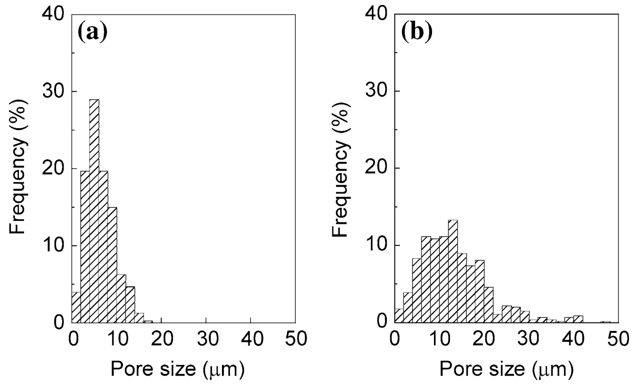

Fig. 5 Pore size distributions of the porous layers formed by exposure of oxynitride glass to humidified O_2 for 500 h at **a** 1153 K and **b** 1183 K

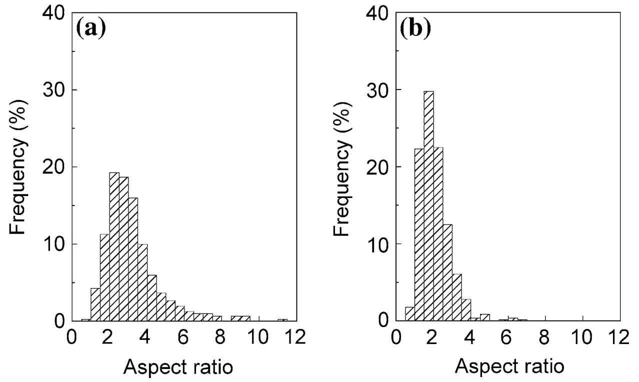

Fig. 6 Aspect ratio distributions of pores in the porous layers formed by exposure to humidified O_2 for 500 h at **a** 1153 K and **b** 1183 K

Table 1 Porosity, average pore size, and average aspect ratio of porous layers formed by exposure of oxynitride glass to humidified O_2 for 500 h

Exposure temperature (K)	Porosity (%)	Average pore size (μm)	Average aspect ratio
1153	64.6	7.0 (3.1)	3.21 (1.50)
1183	43.4	15.5 (7.7)	2.09 (0.80)

Standard deviation are shown in brackets

The concentration in a unit volume of N_2 gas, which is generated by water vapor corrosion of the oxynitride glass, is constant. Assuming that the N_2 gas behaves as an ideal gas, then according to the ideal gas law, the pressure of the N_2 gas will be directly proportional to the exposure temperature. However, the gas pressure was slightly increased with the increase of the exposure temperature from 1153 to 1183 K. The production of porous glass layer caused by the foaming of N_2 gas in the glass would mean that the morphology of the pores is strongly affected by the viscosity of the glass. The glass is deformed more easily at 1183 K than at 1153 K, and therefore the pore sizes increased according to the increase in the exposure temperature. In addition, the deformation of the glass is considered to be suppressed more strongly at 1153 K than at 1183 K in the direction parallel to the glass surface, owing to the difference of the glass viscosity. As a result, the gas generated in the glass tends to be expanded toward the direction normal to the surface with decreasing the exposure temperature, and therefore pores produced by exposure at 1153 K may have larger aspect ratio compared with that at 1183 K, as indicated in Fig. 6 and Table 1.

The porous glass specimen (200 μm thick machined specimen) obtained by exposure to humidified O_2 at 1183 K for 500 h demonstrated gas permeation properties via measurement of the flow rate of N_2 gas under differential pressure across the porous layer. The result suggests that the porous layer is composed of three-dimensional continuous pores. In addition, the superficial velocity of the sample was proportional to the differential pressure, as shown in Fig. 7. The permeability constant, k, of the specimen can be determined from the relationship between the flow rate and the applied N_2 pressure, according to Darcy's law [10],

$$k = \frac{Lu\mu}{\Delta P} \tag{1}$$

where ΔP is the differential pressure across a specimen of thickness L. Assuming that the superficial velocity, u, of the gas with viscosity of N_2, μ, was the same throughout the specimen, the permeability constant was determined to be 3×10^{-16} m^2 and the correlation coefficient (R) was 0.999.

Figure 8 shows the porous layer formed by exposure to humidified O_2 at 1173 K for 500 h, followed by treatment at 1143 K for 1000 h. The resulting porous layer has a graded structure with different morphological characteristics and the porous structure obtained by the former heat-treatment was held until after the latter heat-treatment. In addition, finer pores were observed at the interface between the corrosion layer and the glass substrate, as shown in Fig. 8. The microstructure of the porous glass layer could be controlled by the exposure temperature and time, so that water vapor corrosion of the oxynitride glass could produce a thin porous glass layer with fine pores and graded pore sizes in the direction of thickness. Therefore, this porous glass may be applied as a filter with lower pressure loss such as a precision filter.

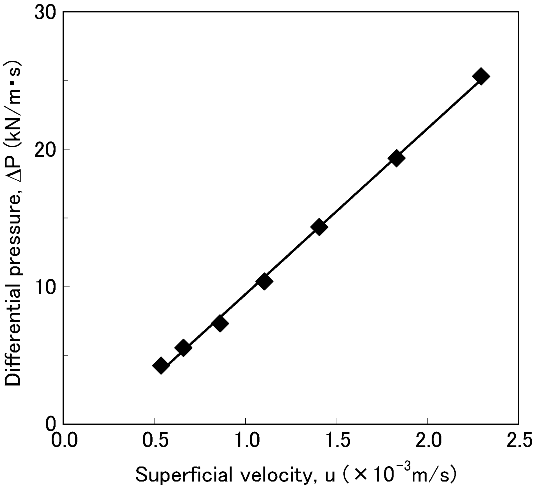

Fig. 7 Dependence of superficial velocity on the differential pressure across the porous layer formed by exposure of oxynitride glass to humidified O_2 at 1183 K for 500 h

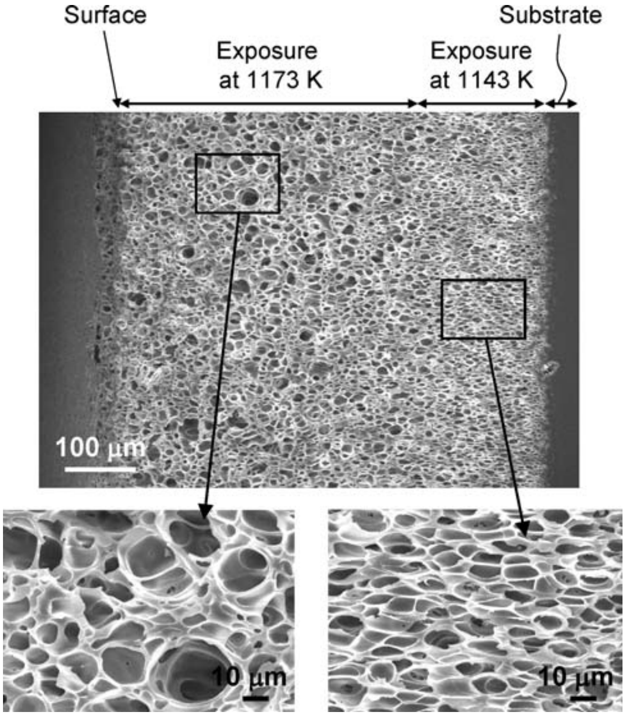

Fig. 8 SEM micrographs of the porous layer formed by exposure of oxynitride glass to humidified O_2 at 1173 K for 500 h, followed by further exposure at 1143 K for 1000 h

Conclusions

A porous glass layer was obtained by exposure of an oxynitride Y–Al–Si–O–N glass to water vapor near the glass transition temperature of the glass. Water vapor plays an important role in the production of the porous layer in the oxynitride glass. When the glass was exposed to dry O_2 gas, a non-porous deteriorated scale layer was observed at the surface. The presence of O_2 in water vapor accelerates the formation of the porous glass layer. The porous scale growth of the oxynitride glass in humidified O_2 near the glass transition temperature followed a linear rate law and the rate-determining step is considered to be the interfacial reaction between the oxide scale and substrate glass. The thickness and average pore size of the porous layer increased with increased exposure temperature, while the aspect ratio of the pores decreased, which is probably related to the decrease in the viscosity of the glass with increasing temperature. A porous glass specimen that was machined from the exposed glass exhibited N_2 gas permeation properties in accordance with Darcy's law, and was therefore considered to be composed of a three-dimensional continuous pore structure. The microstructure of the porous corrosion layer could be controlled by the exposure temperature, so that the oxidation of oxynitride glass by the humidified gases could produce porous glass with graded microstructures according to the size, porosity, and aspect ratio of the pores.

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