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# Large-scale production of alkali-resistant Shirasu porous glass (SPG) membranes: Influence of $ZrO_2$ addition on crystallization and phase separation in $Na_2O$–CaO–$Al_2O_3$–$B_2O_3$–$SiO_2$ glasses; and alkali durability and pore morphology of the membranes

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ABSTRACT

To develop the large-scale production of alkali-resistant Shirasu porous glass (SPG) membranes based on phase separation and subsequent acid leaching, the crystallization and phase separation in mother glasses in the NaO–CaO–$Al_2O_3$–$B_2O_3$–$SiO_2$ system containing $ZrO_2$ were investigated. A crystalline phase of wollastonite ($CaSiO_3$) was formed in the $ZrO_2$-free mother glass heat-treated at approximately 900 °C, corresponding to the glass-shaping temperature. This crystallization was induced by the phase separation in the mother glass. The crystallization tendency was reduced by adding $ZrO_2$ to the mother glass due to an increase in the glass viscosity, and there was no crystallization in the mother glass with 3.5 mol.% $ZrO_2$. SPG membranes containing 3 mol.% $ZrO_2$ were successfully prepared from the mother glass with 3.5 mol.% $ZrO_2$ by the phase separation of the mother glass at 700–760 °C and subsequent acid leaching with a 0.5 mol $dm^{-3}$ hydrochloric acid. The membranes had an interconnected pore structure over a wide pore diameter range of 0.1–10 μm. The membrane pore diameter increased with increasing heat-treatment temperature and holding time during the phase-separation process for the mother glass. The alkali resistance of the membranes was about 3.5 times higher than that of conventional SPG membranes.

## 1. Introduction

Porous glass membranes are prepared based on phase separation and subsequent acid leaching [1–6]. The outstanding advantages of porous glass membranes over porous polymeric and ceramic membranes are the narrow pore size distribution and a wide range of available pore sizes [2–4,7,8]. Porous glass membranes find many applications as a separation membrane [9–18], a demulsification medium [19], a gas–liquid membrane contactor [20], and especially as a dispersion medium in both membrane emulsification [21–25] and gas dispersion process [26,27] for the formation of uniformly sized droplets, and nano-/micro-bubbles. With membrane emulsification or gas dispersion process, one immiscible phase (liquid or gas) is forced through an SPG membrane into the other immiscible liquid phase in the presence of surfactant to form uniformly sized droplets or nano-/micro-bubbles.

The phenomenon of phase separation, necessary for the preparation of porous glass membranes, has been found in several glass systems. Phase separation in glasses occurs based on two mechanisms [5]: nucleation and growth; and spinodal decomposition. In the nucleation/growth process, one glassy phase forms a droplet phase, and the other phase forms a matrix phase. The phase separation caused by spinodal decomposition process provides interconnected two-phase structure. The size of the domains of the two phases increases with increasing temperature in the range from the glass transition temperature to the consolute (or critical) temperature, above which no phase separation occurs or the two phases become identical. The main factor affecting the morphology of phase separation is the chemical composition of the glass system. The droplet-type morphology is found for chemical compositions near the sides of liquid–liquid immiscibility region, while the interconnected-type morphology is found for compositions near the center of immiscibility region. In many cases the separated two phases differ in chemical resistance each other. For the phase separation caused by spinodal decomposition, one of the separated phases can be leached out with acid solutions. This phenomenon is used for the preparation of porous glass membranes. The molten glass is drawn into a tube, and then thermally

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treated at temperatures between the glass transition temperature and the consolute temperature to separate into acid-soluble and acid-insoluble phases. The consolute temperature is defined as an upper temperature at which separated phases are thermodynamically stable, or as the lowest temperature at which a single phase is thermodynamically stable. Subsequently, the acid-soluble phase is leached out with an acid solution, resulting in a porous glass membrane with an interconnected pore structure. During the heat-treatment process, a careful temperature control leads to a narrow pore size distribution of the resultant membrane. The pore size of the glass membrane is controlled by adjusting the phase-separation conditions (the temperature and holding time) during the heat-treatment process.

The first investigation on porous glass membranes can be dated back to the 1930s, in which glass membranes were developed as precursors of high siliceous glasses by Hood and Nordberg [2–4]. Porous glass membranes of this type, known as 'Vycor® glass membranes' [2–4], are prepared based on the phase separation of $Na_2O$–$B_2O_3$–$SiO_2$ type glass. The mother glass is heated at temperatures between 550 and 600 °C, and thus allowed to separate into an acid-insoluble, silica-rich phase and an acid-soluble, borate phase. The borate phase is then removed by acid leaching to leave a porous silica-rich phase, resulting in a porous Vycor® glass membrane with nano-sized uniform pores. Vycor® glass membranes have been widely investigated for membrane separation including nano-/ultrafiltration and gas separation [9–11,14,15]. A disadvantage of Vycor® glass membranes is the relatively poor chemical durability due to their high silica content (approximately 96 wt.%) and large specific surface area [28]. When a glass membrane is exposed by a strong alkali solution, the Si—O bonds of the glass network in the membrane skeleton break due to the attack of $OH^-$ ions, and thus the silica network is gradually destroyed [29]. As a result, the remaining glass components are released, resulting in total glass dissolution and larger pore size. Furthermore, Vycor® glass membranes are soluble even in water at room temperature because the main glass component of $SiO_2$ has a water solubility of approximately $100\,g\,m^{-3}$ [30]. For this reason, the industrial membrane applications of Vycor® glass membranes for aqueous systems have been limited.

Shirasu porous glass (SPG) membranes [8,31] are another type of glass membranes, which have been developed in the 1980s and are made from $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ type mother glasses, which can separate into an acid-soluble (silica-rich) phase and an acid-soluble (borate-rich) phase. Shirasu used as a source of $SiO_2$ and $Al_2O_3$ for the mother glass is a volcanic ash widely available in the southern part of Kyushu Island in Japan [31]. The pore diameter of SPG membranes is controlled over a range from several tens of nanometers to several tens of micrometers by adjusting the phase-separation conditions. Over the past two decades, SPG membranes have been extensively investigated as a dispersion medium in emulsification and gas dispersion processes [21–27] and as a separation membrane for ultra- and microfiltration [13,17,18]. The main difference between Vycor® glass and SPG membranes is the chemical composition. SPG contains $SiO_2$ of about 70 wt.%, $Al_2O_3$ of 10–15 wt.%, and other minor components [8]. Due to the relatively higher $Al_2O_3$ content, SPG membranes show extremely high water resistance. Nevertheless, their chemical durability against alkali solutions is relatively poor because of the relatively higher $SiO_2$ content in the glass skeleton. In many membrane applications, membrane cleaning is significantly important because membrane fouling leads to a drastic reduction of transmembrane flux, and thus periodic cleaning of the membrane is needed. However, it is difficult to clean SPG membranes with strong alkali agents after fouling due to their poor alkali durability. On the other hand, it is known that increasing content of $ZrO_2$ in silicate glasses significantly improves the chemical durability against alkali solutions [28]. The $ZrO_2$ addition allows the covalent Zr—O—Si bonds to be formed in the silicious glass network, and thus strengthen the silica network. To prepare SPG membranes with alkali durability, the component of $ZrO_2$ must be distributed in the acid-insoluble phase, which corresponds to the resultant porous glass. However, it should be noted that the introduction of $ZrO_2$ to the composition of mother glass leads to a slower growth rate of phase-separated structure due to an increase in the glass viscosity [32,33]. With regard to both the phase separation of mother glass and the alkali durability of the resultant SPG membrane, the optimal content of $ZrO_2$ should be clarified. The first objective of this study is to improve the alkali durability of the membranes by introducing $ZrO_2$ into the glass skeleton of SPG membranes. Alkali-resistant SPG membranes were prepared from a mother glass in the $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ system containing $ZrO_2$. Over the past two years, several studies have been made on the preparation of alkali-resistant porous glasses from $ZrO_2$-containing borosilicate glasses [28,33–35], which were basically composed of $RO$–$B_2O_3$–$SiO_2$ (R = Mg, Ca, Sr, Ba and Zn) [28], $Na_2O$–$B_2O_3$–$SiO_2$ [33] and $Na_2O$–$B_2O_3$–$Y_2O_3$ [34] glass systems. This investigation is the first attempt to use $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ glass systems containing $ZrO_2$ to develop alkali-resistant porous glass membranes. Advantages of the use of this glass composition are the excellent shaping ability and a wide range of available pore sizes of the resultant membranes [8,36].

Besides the poor alkali durability, the high cost is another disadvantage of SPG membranes. Along with the active applications on SPG membranes, there is an increasing need for the mass production of SPG membranes with lower cost because they have been manufactured by the hand-production process, which leads to a high manufacturing cost. To overcome this problem, it is necessary to develop the machinized shaping process of the mother glasses used as precursors of SPG membranes. However, during the glass-shaping process, crystalline phases are frequently formed because the mother glass must be held for a long period at an elevated temperature (about 900 °C). This undesirable phenomenon is known as 'devitrification', which is the uncontrolled formation of crystalline phase in a glass on heating to temperatures ranging from its glass transition temperature to its liquidus temperature because crystalline phases are thermodynamically more stable than glassy phase [37]. The devitrification on the mother glass causes the resultant SPG membranes of significantly poor quality. Conventionally, the mother glasses have been formed into tubes by the hand-production process such as the blowing process [36], in which the mother glass is melted in a pot, and then is formed into tubes with a blowing pipe. With this blowing method, the shaped glasses are immediately cooled to room temperature, resulting in a suppression of devitrification on the mother glass tubes. However, the mother glass tubes cannot be produced on a large scale, and thus the resultant SPG membranes become expensive. The second objective of the present study is to avoid the devitrification on the mother glass during the machinized glass-shaping process needed for the mass production of SPG membranes. The glass devitrification is strongly affected by the chemical composition of the mother glass. Small amount of certain additives including $ZrO_2$ may induce an increase in glass viscosity or a decrease in ion mobility, reducing the crystallization rate [38]. In this investigation, to prevent the glass devitrification during the machinized glass-shaping process, $ZrO_2$ is added to the composition of a mother glass in the $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ system, which has been conventionally used for the preparation of SPG membranes.

This study presents the influence of $ZrO_2$ added to the composition of $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ glass on both the crystallization of the mother glass and the alkali durability of the resultant SPG membrane. The influence of $ZrO_2$ addition on the pore morphology of the resultant SPG membranes is also reported.