ALKALI-FREE GLASS-CERAMIC RIGID MEMBRANES

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A process is proposed for the manufacture of alkali-free glass-ceramic rigid membranes of varying selectivity. The physiomechanical properties of the membranes are described. The membranes can remove microorganisms from polluted water with an efficiency of 95 to 98%.

Fundamentally new technologies, novel materials, and novel sources of energy are needed to achieve the new objectives set by modern industry. In chemical engineering, a special place in this respect is taken up by membrane technology [1].

The polymer membranes widely used in membrane separation do not always possess the necessary properties, such as thermal stability and chemical stability essential in some operations, and capacity for regeneration. To fill the need, work has of late been stepped up on new types of inorganic membranes which offer a number of advantages. Among them are corrosion and abrasion resistance, mechanical strength, resistance to bacteria, thermal stability, ability to operate over a wide range of pH values, capacity for regeneration by steam, chemical reagents and thermal treatment, and longer service life.

One way to make inorganic membranes is to use alkali-free crystallizing glasses. Almost nothing is known about porous structures fabricated from crystallizing glasses [2]. However, the possibility of making rigid membranes by a relatively simple process and at relatively low sintering temperatures is undoubtedly of interest, and the high physiomechanical properties of parent glasses and glass ceramics are bound to assure good mechanical, thermal, chemical and other properties in the membranes made from them.

We undertook a study which had as its objective to make various porous structures from a glass ceramic material in the system SiO₂ – TiO₂ – Al₂O₃ – CaO – BaO – B₂O₃ in the form of powders widely differing in grain-size analysis. The compositions and properties of the glass ceramics in this system are described in a monograph [3]. Their principal crystalline phases are celsian, anorthite, and rutile.

The materials in our study were fabricated from glass-ceramic powders with particle sizes smaller than 50 μm (fraction I), 50 – 63 μm (fraction II), and 63 – 80 μm (fraction III).

The scheme by which rigid porous structures can be made from a glass-ceramic material is as follows: The parent crystallizable glass is melted at 1480 – 1500°C and held at the maximum temperature for 1 h → the glass is allowed to crystallize at 750°C for 1 h and at 1060°C for 1 h → the glass ceramic is ground to a powder → the powder is separated into various grain sizes → the screened powder is sintered in ceramic molds.

The key advantage of the process is that there is no need for any bonding agent, organic or inorganic. The necessary bonding action in the porous structure is provided by the retained glass phase which accounts for 30 – 40% of the total [3, 4].

After crystallization and the formation of crystalline phases (anorthite, β-celsian, and rutile), the retained glass is
enriched with SiO₂ and Al₂O₃, which improves its chemical and thermal properties and has a positive effect on the characteristics of the end product.

To choose the optimal sintering temperatures and durations, we analyzed how the shrinkage of the specimens and their flexural and compressive strength varied with the sintering temperatures (Figs. 1 and 2).

The analysis of specimen shrinkage, which has a strong bearing on the manufacture of rigid membranes and their mechanical properties, revealed that a porous structure of the best quality was formed for shrinkage of 6 – 7%. This was an important consideration in choosing the sintering conditions. As experiments demonstrated, with shrinkage of about 10%, the specimens acquired a structure almost devoid of pores or of very low porosity.

Sintering in the manufacture of rigid membranes is governed by many factors. Those of special importance are the total effective contact surface energy, relative orientation of contact surfaces, diffusivity and viscosity of the retained glass phase, shear stresses, vapor pressure, evaporation rate, interatomic binding forces, and surface activity [5]. Sintering as used in the manufacture of structural ceramics from pure oxide microgranules produced from melt and a finely divided powder can be liquid-phase and solid-phase. As shown in [5], the strength of a fritted ceramic material can be controlled by giving the granules the desired shape.

Synthetic membranes usually have a simple structure [1] and operate by well-known mechanisms. Therefore, it is important to consider the inverse problem — production of more complex composite structures with better functional capabilities from elementary membranes.

Glass-ceramic specimens must possess optimal porosity and strength.

As can be seen from Fig. 2, in the specimens prepared from fraction I an increase in the sintering temperature was accompanied by a sharp increase in both the bending and the compressive strength, and the latter was at its highest at a heat-treatment temperature of 1030°C.

The strength of fraction II and III specimens varied with an increase in the sintering temperature in a similar manner. This implies that the increase in strength was mainly due to the glassy phase that binds the grains of the glass-ceramic powder. Importantly, the melt of the glassy phase and the decrease in its viscosity depended on the sintering temperature and on the holding time at that temperature. The decisive factor was, however, the temperature and not the holding time, as can be clearly seen from the behavior of the curves in Fig. 2.

It was found by experiment that in the fraction I specimens, the porosity sharply decreased at a temperature higher than 1030°C and fell to almost zero at 1040°C. In the fraction II and III specimens, this occurred at 1170 – 1180°C (Fig. 3).

An examination of the specimens for strength revealed that every fraction needed a sintering schedule of its own, suitably matched to produce a porous structure, on the one hand, and to assure the best possible strength characteristics, on the other.