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Preparation of Glass-Impregnated Isotropic Graphite and its Gas Permeability

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Abstract

Two kinds of borosilicate glass, T1 (SiO_2: 38%, B_2O_3: 36%, Na_2O: 21%, Al_2O_3: 5%, softening point 620°C) and T2 (SiO_2: 50%, B_2O_3: 30%, Na_2O: 15%, MgO: 5%, softening point 639°C), were impregnated into a high-density isotropic graphite block. Achieved impregnation depths were 50 and 24 mm for glasses T1 and T2, respectively, with typical impregnation conditions of 1200°C and 15 MPa pressure for 1 h. Around 90% of the open pore volume of the original graphite was occupied by the glass. Gas permeability of the T1- and T2-impregnated graphites was reduced to $6{\cdot}2 \times 10^{-5}$ and $1{\cdot}8 \times 10^{-6}$ cm^2 s^{-1}, respectively, from $1{\cdot}3 \times 10^{-1}$ cm^2 s^{-1} for the original untreated material. Glass impregnation was shown to be more effective in reducing gas permeability than phenolic resin. It was suggested that gas permeability could be much reduced by minimizing the machining of the glass-impregnated blocks.

1 Introduction

Isotropic graphite materials are widely used because of their fine texture, high strength and excellent thermal stability. However, they are gas permeable due to the pores which are unavoidably created in the production process. There is a strong demand to make isotropic graphite impermeable to gases for many applications. Impregnation of synthetic resins and metals with low melting point into the pores of graphite has been commonly performed in order to lower permeability.[1] It can be important to impregnate the graphite with high melting point materials for applications where thermal stability is required, though this needs high pressures and temperatures. Impregnation of borosilicate glass into a low-density graphite electrode nipple has, for example, been reported.[2] We have tried to impregnate borosilicate glasses into dense carbon and graphite materials by using an autoclave capable of high pressures and temperatures.[3–5]

In the present paper, we investigate the process and conditions for the impregnation of two kinds of borosilicate glass into a high-density isotropic graphite to provide gas impervious materials.

2 Experimental Procedures

2.1 Materials

A high-density isotropic graphite, grade IG-11 manufactured by Toyo Tanso Co., Ltd, was used as a graphite substrate. Its properties are tabulated in Table 1. It was made from a petroleum coke with average grain size of 10 μm, and its open porosity was ~15% with a mean pore radius of 1·7 μm. Two kinds of borosilicate glass, which are here termed T1 and T2, were selected for impregnation. Their composition and physical properties are summarized in Table 2. The composition of these glasses was designed so that they would have a reasonably small difference in thermal expansion coefficient from graphite. The temperature dependence of viscosity for these glasses is shown in Fig. 1. A higher content of SiO_2 in glass T2 results in higher thermal and chemical stabilities, and also in higher viscosity than for T1.

2.2 Apparatus and conditions for impregnation

An apparatus for glass impregnation is illustrated in Fig. 2. This facility is capable of working either in vacuum or under a pressure of up to 15 MPa nitrogen gas and at temperatures up to 1500°C. The impregnant is loaded in a crucible and the pieces of graphite are placed in a sagger attached to the upper lid. Raising and lowering of the lower actuator allows the pieces to be immersed or separated from the molten impregnant. A flow chart of the impregnation procedure employed in the present work is shown in Fig. 3(a).

Table 1. Mechanical properties of the original and borosilicate glass-impregnated graphites

	Bulk density (g cm^{-3})	*Shore hardness*	*Bending strength (MPa)*	*Compressive strength (MPa)*	*Young's modulus (GPa)*	*Thermal expansion coefficient (10^{-6} K^{-1}), 350–450°C*
Original graphite (IG-11)	1·78	56	40	77	10·5	4·6
Glass T1-impregnated	2·08	70	58	147	17·3	5·8
Glass T2-impregnated	2·09	68	61	154	17·7	5·5

Table 2. Composition and properties of borosilicate glasses for impregnation

Glass	*Composition (mass %)*					*Glass transition point (°C)*	*Softening point (°C)*	*Thermal expansion coefficient (10^{-6} K^{-1}), 50–300°C*	*True density (g cm^{-3})*
	SiO_2	*B_2O_3*	*Na_2O*	*Al_2O_3*	*MgO*				
T1	38	36	21	5	—	513	620	9·6	2·49
T2	50	30	15	—	5	521	639	9·3	2·50

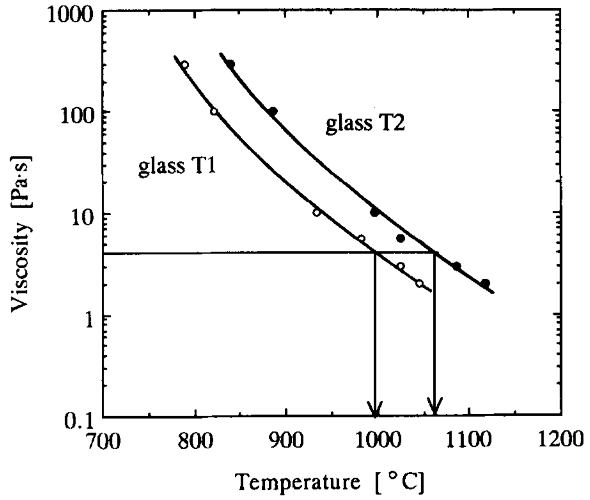

Fig. 1. Temperature dependence of viscosity of borosilicate glasses for impregnation.

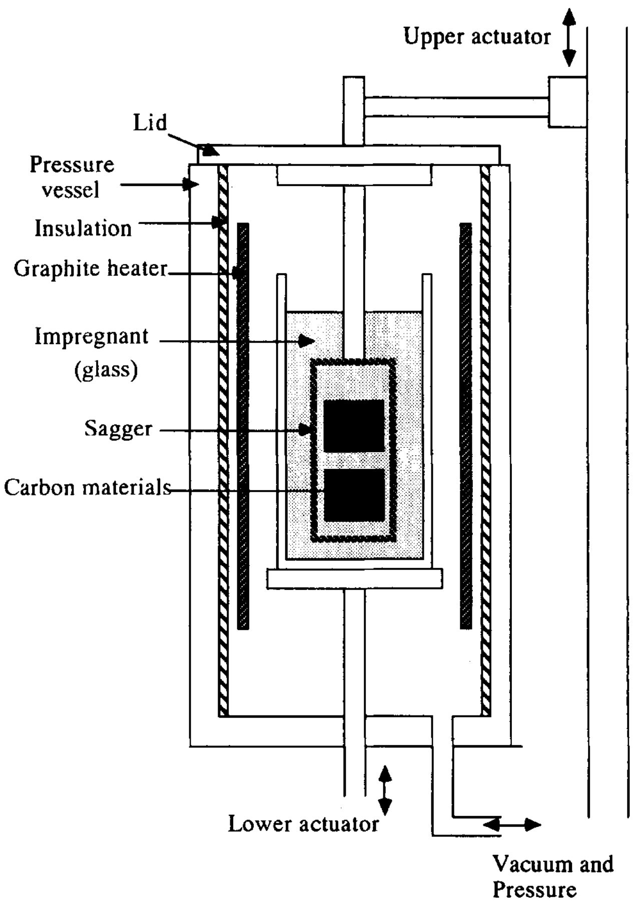

Fig. 2. Autoclave for glass impregnation.

The impregnation of glass T1 into graphite IG-11 was carried out at temperatures of 1000, 1100 and 1200°C under a pressure of 15 MPa for 1 h. The impregnation of glass T2 was carried out at a temperature of 1200 °C under the same pressure as in the case of T1. A typical temperature programme during impregnation is shown in Fig. 3(b). The autoclave was kept in a vacuum ~0·13 kPa in order to evacuate gas from the graphite blocks and glass. The ramp-up rate was slowed down from 400° h^{-1} to 200° h^{-1} at 800°C to promote smooth gas evacuation. The final temperature was held for 1 h to produce a uniform temperature distribution in the molten glass before immersing the sample graphite. After the immersion of the graphite blocks into the molten glass by raising the crucible, the pressure was increased to 15 MPa and held at this value for 1 h. To study the impregnation depth of the glass into the graphite, a cubic block of 100 × 100 × 100 mm^3 size was used, two opposite faces of which were protected from glass impregnation by a carbon sheet. After impregnation, the block was cut into two pieces and the depth of glass impregnation was measured by spreading grease on the cut surface of one piece; after wiping it off with an organic solvent, the non-impregnated surface gave different results from that of the impregnated part. Mechanical properties of the impregnated samples were measured by conventional methods and the open porosity was also determined by mercury porosimetry. Test specimens for the measurements were taken from the glass-impregnated graphite, after the surface layer of about 5–10 mm had been cut off.

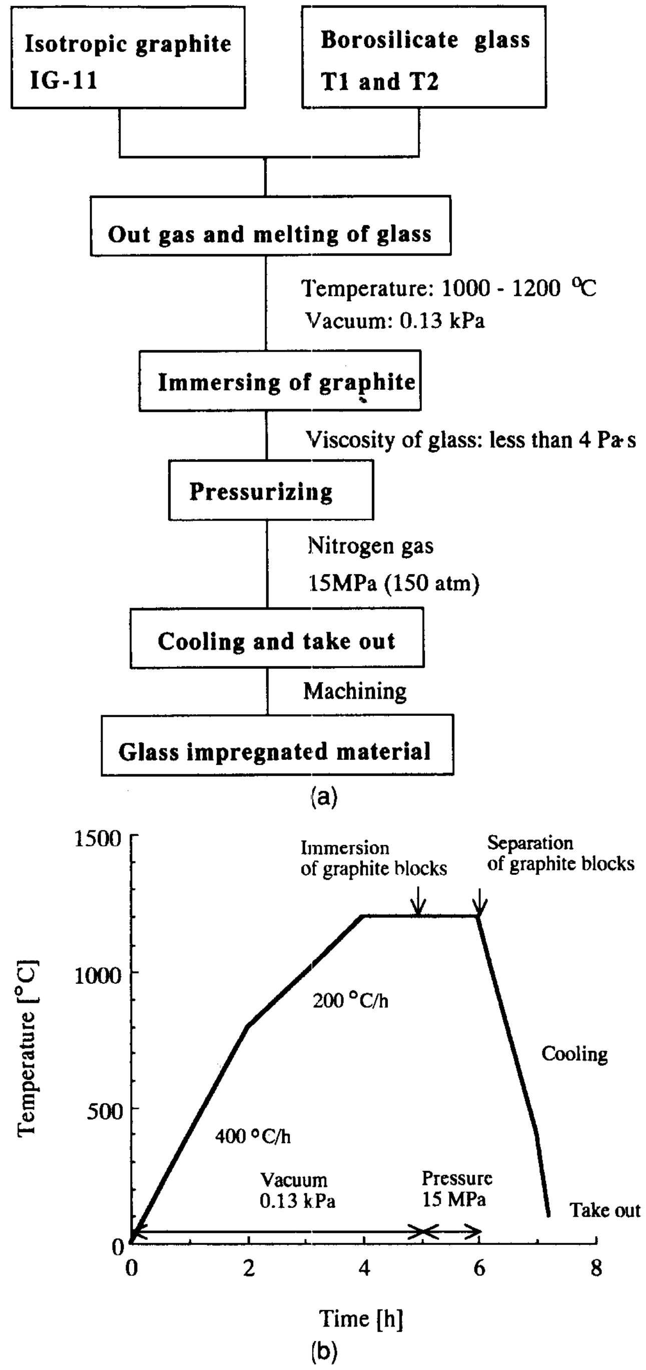

Fig. 3. (a) Flow chart of glass impregnation procedure. (b) Typical temperature programme for glass impregnation.

Impregnation of phenolic resin into the graphite substrate was also carried out. Curing of the resin was done at 200°C. A hollow cylindrical test specimen with an inner diameter of 5 cm, an outer diameter of 8 cm and 4 cm length was taken from a phenolic resin-impregnated block. A second impregnation was conducted on the test specimen, and no machining was done because no resin remained on the surface after the impregnation.

2.3 Measurement of gas permeability

Gas permeability K [cm^2 s^{-1}] was calculated from the following equation:[6,7]

$$K = QL / \Delta PA \tag{1}$$

where Q [Pa cm^3 s^{-1}] is the flow rate of permeated gas, L [cm] is the thickness of the specimen, ΔP [Pa] is the pressure difference in the two chambers separated by the specimen and A [cm^2] is the cross-sectional area for gas permeation. The value Q was determined by the rate of pressure rise and by the volume of the secondary chamber into which gas permeated through the specimen from the primary chamber, which was kept at 100–600 kPa. Details of the equipment used for the present measurements have been reported elsewhere.[8,9]

In the present work, the permeability specimens were cut from 100 mm cubic glass-impregnated blocks and the size of the specimen is a disc, 3 cm in diameter and 0·7 cm in thickness. In the present equipment, the gas permeation diameter is set at 2 cm, so that A is 3·14 cm^2 and L is 0·7 cm in eqn (1). The measurement was done at room temperature using nitrogen gas of high purity.

The gas permeability K of graphite materials has been reported to be approximated by the following relation:[6,7]

$$K = (B_O/\eta)\, P_m + (4/3)K_O(8RT/\pi M)^{1/2} \tag{2}$$

where B_O [cm^2] is the viscous flow permeability, K_O [cm] is the molecular flow coefficient permeability, η [Pa s] is the viscosity of the gas, P_m [Pa] is the mean pressure of the two chambers, R [cm^3 Pa mol^{-1} K^{-1}] is the gas constant, T [K] is the temperature and M [kg mol^{-1}] is the molecular weight of gas. The contribution of molecular flow gas permeation through pores in the specimen was assessed from the relation between K and P_m.

To see the effect of machining, a hollow cylindrical graphite block with an inner diameter of 5 cm, an outer diameter of 8 cm and 4 cm in length was also impregnated by glass T1. The impregnation was carried out at a temperature of 1200°C under a pressure of 15 MPa for 1 h. After impregnation, the glass adhering to the surface was removed carefully by using a file and sandpaper and the surface skin of ~0·05 cm was cut off using a lathe. In the gas permeability measurement with the cylindrical specimen, gas permeated from the outer wall to the inner wall. In eqn (1), A was taken as the logarithmic mean of the inner and the outer wall surface area, and L is the thickness of the cylinder. Both nitrogen and helium gases were used for this measurement.

3 Results and Discussion

3.1 Glass impregnation

It was found that the viscosity of the molten glass should be lower than 4 Pa s to allow smooth mechanical immersion of the sagger into the molten

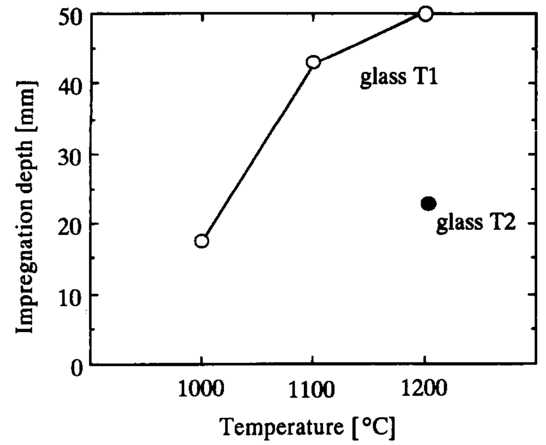

Fig. 4. Relations between impregnation depth into IG-11 graphite and temperature for glass impregnation (pressurized at 15 MPa for 1 h).

glass. For glass T1, a temperature above 1000°C where its viscosity becomes ~4 Pa s was necessary, as shown in Fig. 1. The maximum temperature was limited to 1200°C to avoid chemical reactions between the glass and the metal crucible. Impregnation depth for the two kinds of glass is plotted against temperature in Fig. 4. Impregnation depth of glass T1 increased significantly with elevation of temperature. At 1200°C, the depth became > 50 mm, which was the measurement limit because the graphite block has a size of 100 mm. However, the impregnation depth for glass T2 was only 24 mm.

The effect of mean pore radius on impregnation depth for glass T1 and T2 into some carbon substrates has been studied in our previous work[3] and is shown in Fig. 5 in the form of curves. Impregnation depths observed on the present substrate IG-11 are also plotted against mean pore radius in Fig. 5, where the impregnation were carried out at a temperature of 1200°C under a pressure of 15 MPa for 1 h. The present data are almost on the curves. This indicates that impregnation depth is very dependent on the pore radius of the materials. Impregnation depth decreases rapidly as the pore radius become small, which suggests that it may be difficult for a material to be fully or deeply impregnated by glass if the pore size is less than 1 μm.

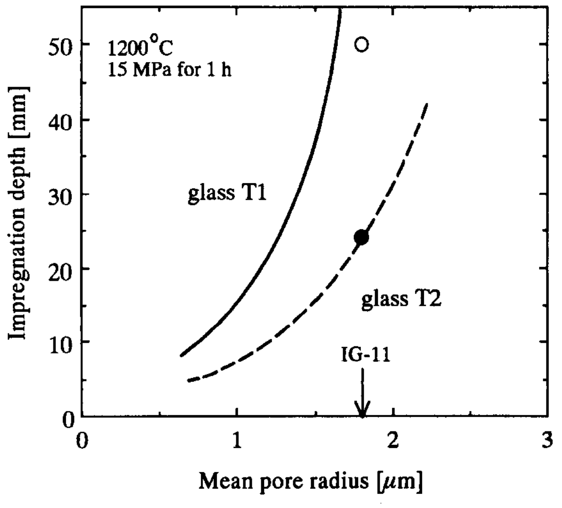

Fig. 5. Relations between glass T1 and T2 impregnation depth and mean pore radius of carbon materials. Impregnation was carried out at 1200°C under a pressure of 15 MPa for 1 h. Open and filled circles are data quoted from Fig. 4.

Micrographs from scanning electron microscopy (SEM) of the polished surface of the original and glass-impregnated graphites are shown in Fig. 6.

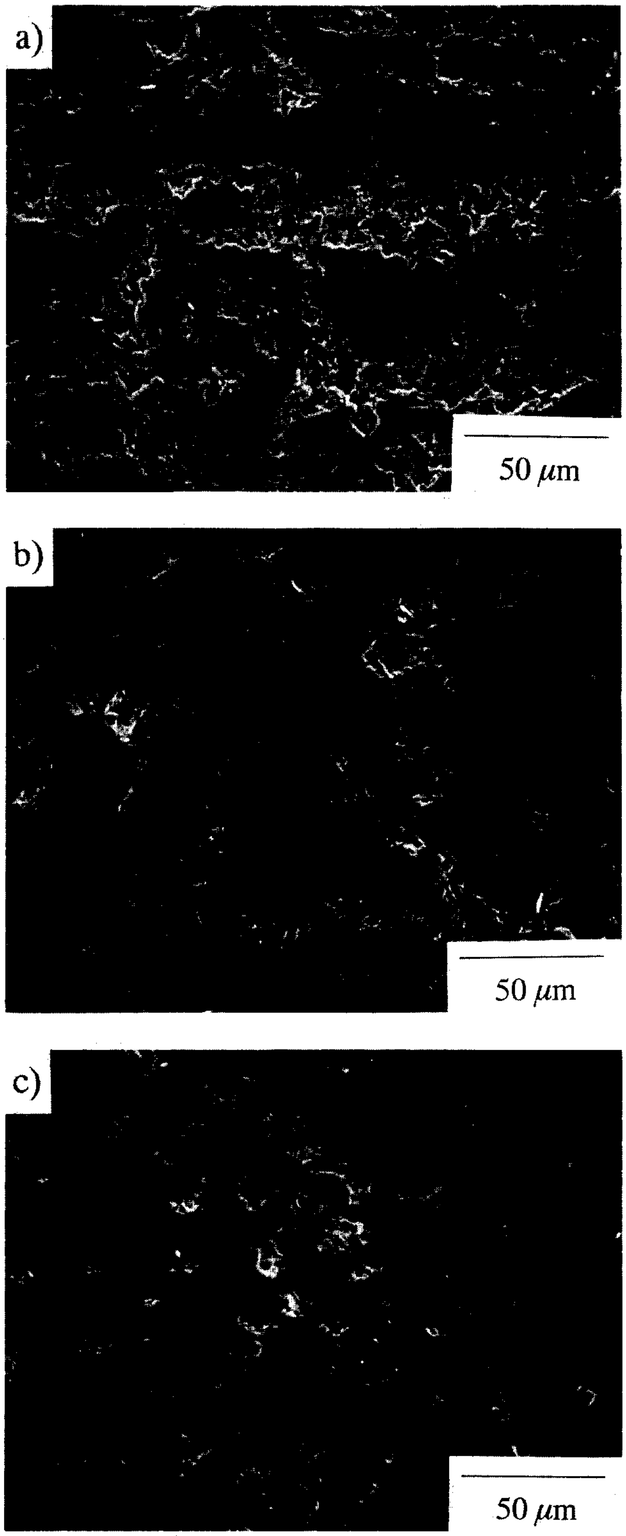

Fig. 6. SEM micrographs of polished surface of the original (a), glass T1-impregnated (b) and glass T2-impregnated (c) graphites.

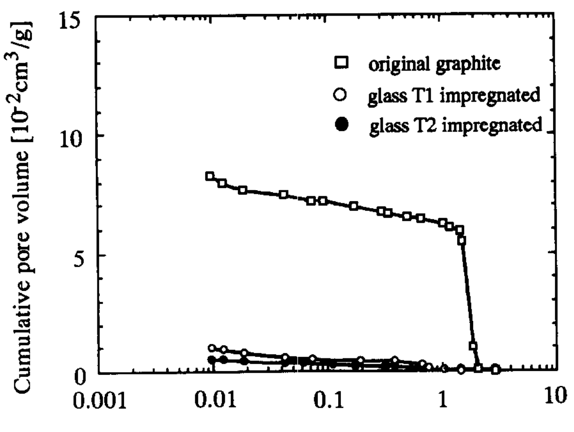

Fig. 7. Effects of glass T1 and T2 impregnation into the isotropic graphite substrate, IG-11, on pore distribution.

Mechanical properties of the glass-impregnated IG-11 are shown in Table 1. The cumulative pore volume of the original and glass-impregnated graphites are determined by mercury porosimetry. These values are plotted against pore radius in Fig. 7.

The SEM micrographs designate that pore regions were much reduced by glass T1- and T2-impregnation. Bending and compressive strengths at room temperature are improved about 1·5 and 2 times by impregnation of the glass, respectively. The Young's modulus becomes about 1·7 times higher than that of the original. A good wettability between glass and graphite is considered to be the main reason for this improvement. Pores of radius > 1 μm disappeared from the graphite substrates following impregnation with both glass T1 and T2. This result means that the size of residual crack-initiating flaws became small. The improvement in bending strength was smaller than that in compressive strength, probably because of the brittleness of the glass. There was no significant difference in mechanical properties between the two glass-impregnated materials. The slightly low thermal expansion coefficient of the T2-impregnated graphite is probably due to the lower thermal expansion coefficient of glass T2 than that of T1.

The volume impregnation ratio was calculated from total open pore volume and density of each material and substrate. About 90% of the open pore volume of the graphite substrate was found to be occupied by the glass.

The voids of ~10% seemed to be mostly pores whose radius was less than 0·7 μm. In the original graphite, the pore volume consisting of pores with radii less than 0·7 μm was ~20% of the total, so that roughly half that region was impregnated. The main reason for residual unoccupied space may be that small pores are difficult to impregnate, as shown in Fig. 5. Also, the larger thermal expansion of these glasses in comparison to that of the graphite substrate results in the creation of space during cooling. It may be noticed that impregnated glass was extruded to a certain extent during cooling by hot gas still confined in the pores; this phenomenon may be more likely to happen if the viscosity of the impregnated molten glass is lower.

The volume impregnation ratio for glass T2 was found to be 93%, which is a little higher than the value of 86% for T1. This finding is probably due to the relatively low thermal expansion coefficient of glass T2 and the relatively high viscosity of glass T2 at the impregnation temperature compared with T1. It was found that glass T2, having a higher viscosity, is more difficult to impregnate deeply, but the impregnated part achieves a slightly higher volume impregnation ratio than T1.

3.2 Gas permeability

The plots of gas permeability K against mean pressure P_m of the original and glass-impregnated graphites are shown in Fig. 8. The K values of the glass T1-impregnated cylindrical specimen whose surface layer was removed to 0·05 cm after impregnation are plotted against P_m in Fig. 9. The viscous flow permeability B_0 and molecular flow coefficient permeability K_0 determined by eqn (2) are summarized in Table 3. In this table, glass-impregnated graphites are compared with phenolic-resin impregnated specimens.

The impregnation of glass T1 and T2 reduced the gas permeability by four and five orders, respectively, from 10^{-1} cm^2 s^{-1} for the original. The low gas permeability of the T2-impregnated graphite seems to result from the high occupation of the open pores by glass T2. It is found that glass impregnation reduces gas permeability more effectively than that with phenolic resin. This is probably due to the fact that condensation gas from the resin creates open pores in the course of curing. By double impregnation of resin, gas permeability was reduced down to 10^{-7} cm^2 s^{-1}, and was independent of pressure; the pore radius being so small that gas flow only by slip on the pore surface is possible.

The gas permeability of the cylindrical specimen was 10^{-7} cm^2 s^{-1} which was lower by two orders of magnitude than that of the T1-impregnated disc after machining. It is supposed that in the vicinity of the surface, glass is well impregnated into the much smaller pores than in the inner part of the block, as Fig. 5 indicates the high dependence of pore radius on impregnation depth. Also, the contribution of the viscous flow of gas for this specimen became much smaller than that of the

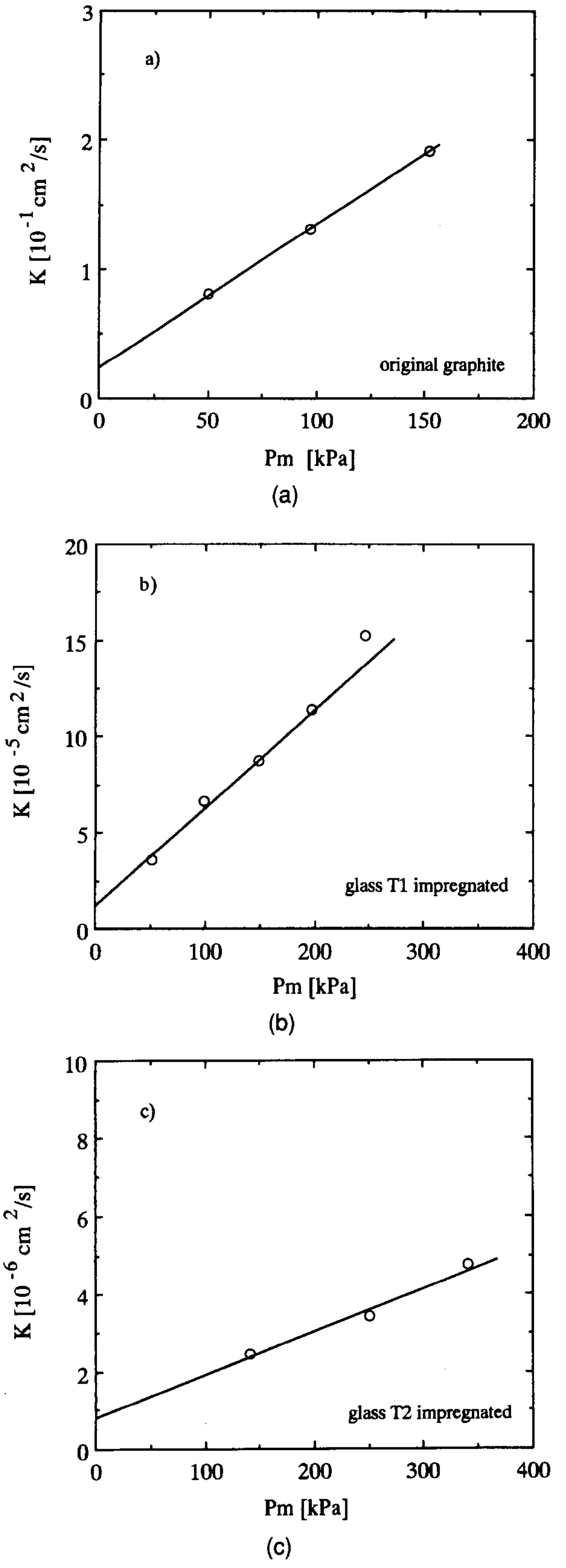

Fig. 8. Relations between gas permeability K and mean pressure P_m of nitrogen gas for the original (a), glass T1-impregnated (b) and glass T2-impregnated (c) graphites.

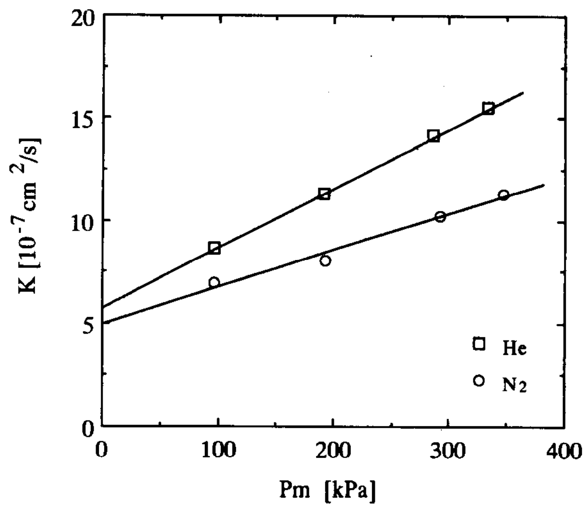

Fig. 9. Relations between gas permeability K and mean pressure P_m of nitrogen and helium gas for a cylindrical specimen whose surface layer was cut off only 0·05 cm after impregnation.

Table 3. Gas permeability and its parameters under nitrogen gas at 25°C for various graphites

	Gas permeability, K *(cm^2 s^{-1})* *(P$_m$ = 98 kPa)*	*Viscous flow permeability,* B$_O$ *(cm^2)*	*Molecular flow permeability,* K$_O$ *(cm)*
Original			
IG-11 graphite	1·3 × 10^{-1}	1·9 × 10^{-11}	1·4 × 10^{-5}
Impregnated			
Glass T1	6·2 × 10^{-5}	9·2 × 10^{-15}	4·5 × 10^{-9}
Glass T2	1·8 × 10^{-6}	2·0 × 10^{-16}	3·5 × 10^{-10}
Glass T1-cylinder*	6·6 × 10^{-7}	3·2 × 10^{-17}	2·4 × 10^{-10}
Phenolic resin once	2·8 × 10^{-4}	4·2 × 10^{-14}	2·0 × 10^{-8}
Phenolic resin twice	2·6 × 10^{-7}	—	1·3 × 10^{-10}

*Surface layer was cut off only 0·05 cm after glass T1 impregnation.

machined specimen; the molecular flow coefficient permeability was close to that of the double resin impregnated specimen, which indicates that the radii of the pores are very small, at least in the vicinity of the surface of the specimen. The gas permeability of helium gas was a little larger than that of nitrogen gas. Gas permeability at constant temperature is only a function of the molecular weight of the gas in the molecular flow dominant region, as indicated in eqn (2), and it follows that helium gas with smaller molecular weight appears to permeate through a porous medium more readily than nitrogen gas. It can be concluded that minimizing of machining is very effective in reducing gas permeability.

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