Table 1. Alkali phosphate glasses : Binding energies and peak area of the O 1s peak (all binding energies in eV).

	O1s(1)	O1s(2)	O1s	bridging	non-bridging(%)
38Li ₂ O-62P ₂ O ₅	533.7	531.7	2.0	37.0(42.5)	63.0(57.5)
36Na ₂ O-64P ₂ O ₅	533.6	531.6	2.0	41.4(43.8)	58.6(56.2)
34K ₂ O-66P ₂ O ₅	533.6	531.6	2.0	47.8(45.1)	52.2(54.9)
(in mol%)	():theoretical value				

Table 2. Sodium phosphate glasses : Binding energies and peak area of the O 1s peak (all binding energies in eV).

	O1s(1)	O1s(2)	O1s	bridging	non-bridging(%)
15Na ₂ O-85P ₂ O ₅	533.9	532.1	1.8	62.2(54.5)	37.8(45.5)
31Na ₂ O-69P ₂ O ₅	533.8	532.0	1.8	45.7(46.8)	54.3(53.2)
36Na ₂ O-64P ₂ O ₅	533.6	531.6	2.0	41.4(43.8)	58.6(56.2)
50Na ₂ O-50P ₂ O ₅	533.1	531.2	1.9	27.9(33.3)	72.1(66.7)
(in mol%)	():theoretical value				

glasses of different composition. It is evident that the area intensity of low energy peak increases with the Na₂O content. **Table 2** shows all data. The O 1s chemical shift of the bridging oxygen atoms increases with increas-

ing Na₂O content.

4. Conclusion

X-ray photoelectron measurements were made on the P₂O₅ glass and the alkali phosphate glasses. From these measurements, the following facts were confirmed quantitatively:

(1) The oxygen ion in the P₂O₅ glass can be divided into the bridging and the double bond states.

(2) The discrimination between bridging and non-bridging oxygen atom in the alkali phosphate glasses is possible.

(3) The cation effect of Li, Na and K in the alkali phosphate glasses is almost same.

(4) The O 1s chemical shift of the bridging oxygen atoms in sodium phosphate glasses increases with increasing Na₂O content.

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ノート・Note

Calculation of Thermal Conductivity in Glass-Copper System by Sphere Packing Models

Mikio IWASA, Makoto KINOSHITA and Ryohei TERAJ

(Government Industrial Research Institute, Osaka, Ikeda-shi 563)

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球充てんモデルによるガラス-銅系の熱伝導率の計算

岩佐美喜男・木下 実・寺井良平

(大阪工業技術試験所)

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The high level radioactive waste from the nuclear reactor is proposed to be incorporated with glass for disposal¹⁾. In that case, the glassy solid must be improved in thermal conduction as well as in other properties to

avoid degeneration, damaging or melting by the radiation energy of the radioactive elements in it. One method to improve the thermal conduction is to combine it with highly conductive materials such as metals.

In the previous paper²⁾, thermal conductivities of glass-copper composite system have been investigated in relation to the content and the morphology of the constituents. In that investigation, two kinds of glass-copper systems were used; one was the mixture system of glass microspheres, GB 733 (average particle size = 66 μm , thermal conductivity of the glass = $1.03 \times 10^{-2} \text{ J/cm} \cdot \text{s} \cdot \text{K}$) and dendritic electrolyzed copper powder, CE 25 (particle size = 5~10 μm , thermal conductivity of copper = $4.1 \text{ J/cm} \cdot \text{s} \cdot \text{K}$), and the other was the mixture system of pulverized glass microspheres, GB 733 and spherical atomized copper powder, At 100 (average particle size = 70 μm). Fully densified composite compacts were prepared by pressure sintering of the powder mixtures. Typical microstructures of the composite compacts are shown in Fig. 1, and the thermal conductivities at around 50°C are also shown in Fig. 2 as a function of the volume fraction of copper together with the theoretical conductivities by Eucken's equation described later.

The microstructures of GB 733-At 100 composites are thought that the copper spheres with high conductivity are dispersed in the glass matrix with low conductivity. So the following equation theoretically derived by Eucken³⁾ can be applicable to predict the conductivity of this system.

$$k = \frac{v_a k_a + v_b k_b / \left(\frac{2}{3} + \frac{1}{3} \frac{k_b}{k_a} \right)}{v_a + v_b / \left(\frac{2}{3} + \frac{1}{3} \frac{k_b}{k_a} \right)} \quad (1)$$

v_a : volume fraction of A (continuous phase)

v_b : volume fraction of B (dispersed phase)

k_a : thermal conductivity of A

(a) GB 733-CE 25 compact

(b) GB 733-At 100 compact

Fig. 1. Typical microstructures of the composite compacts containing 40 wt% Cu. (a) GB 733-CE 25 compact, (b) GB 733-At 100 compact

Fig. 2. Measured thermal conductivities of glass-copper composite compacts.

k_b : thermal conductivity of B

k : thermal conductivity of the composite

As seen in Fig. 2, the agreement between the experimentals and the theoreticals seems excellent in the region of the copper content up to about 20 vol%. Beyond this content, discrepancy becomes apparent as the results of the rapid increase in thermal conduction by the contact taking place between the copper spheres. The equation proposed by Budiansky⁴⁾ gives practically the same results as Eucken's equation.

The microstructures of GB 733-CE 25 composites are thought that the copper is intruding between the glass microspheres and seems almost continuous if the copper content becomes large enough. The thermal conductivity of this system rapidly increased with increasing copper content as seen in Fig. 2. However, Equation (1) can not be applied in the region of interest because both of the constituents are thought to be continuous in the composites having low copper content, and theoretical

prediction of the conductivity about this system is almost impossible due to the difficulty in solving the differential equations on thermal conduction.

There is a general empirical equation on physical properties of mixture system :

$$k^n = v_a k_a^n + v_b k_b^n \quad (2)$$

Using this equation, it may give the conductivities consistent with the experimentals if we put $n=0.2\sim0.3$. But this equation is not suitable to predict the conductivity as the exponent, n , must be changed with the copper content and the physical meaning of this equation is not clear.

About the composite system such as GB 733-CE 25 system, we made up model structures and calculated the thermal conductivity based on some assumptions. The glass spheres are arranged like crystal structures such as simple cubic lattice (sc), body centered cubic lattice (bcc) or face centered cubic lattice (fcc), and the copper occupies the interspaces between the glass spheres. Thermal conductivity was calculated on the primitive cell of the lattice in the direction of maximum packing as follows. The primitive cell is cut into many thin slabs perpendicular to the direction of heat flow, and the conductivity of the slab is calculated as a parallel junction of glass and copper with an assumption that copper does not occupy the interspace at the slab when the ratio of the spacing between the glass spheres to the diameter of the glass sphere becomes less than a certain value, R . Then the thermal conductivity of the primitive cell is calculated as a series junction of these thin slabs. **Figure 3** illustrates sc model.

This procedure can be expressed by the following integral formula.

$$\frac{1}{k} = \int \frac{dx}{s_a k_a + s_b k_b} / \int \frac{dx}{s_a + s_b} \quad (\text{if } d_a/d_b < R, k_a=0) \quad (3)$$

x : direction of heat flow

Fig. 3. Schematic illustration of sc model and cross sections.

- s_a : sectional area of A (matrix, copper), function of x
- s_b : sectional area of B (sphere, glass), function of x
- d_a : maximum spacing between B spheres, function of x
- d_b : diameter of B sphere, constant
- R : critical ratio, given constant

We think this integral is the conductivity of the composite having the microstructure like GB 733-CE 25 system. The results of the computation about the composite system are shown in **Fig. 4** for sc and fcc models. sc and bcc models are found to be inadequate, and the results from these models do not agree with the experimentals. fcc models can give a good agreement in the region of copper content up to about 15 vol%, if the critical ratio is assumed to be $1/8$ to $1/7$. This critical ratio is in good coincidence with the ratio of the particle size at the tail of size distribution

Fig. 4. Computed results with various critical ratios and the experimentals. Solid line: theoreticals, Dashed line: experimentals.

(a) sc model, (b) fcc model

of copper powder to the average particle size of glass microspheres. This would be reasonable on the basis that the interspaces smaller than the fine copper particles are not likely to be filled up by copper in the actual compacts.

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訂 正

窯業協会誌 88 [6] (1980) 掲載の、加藤哲郎他、“窒素 1 気圧中、1600°C における Cr-B-N 系の反応及び相関係”の本文中に誤りがありましたので、下記のように訂正致します。

項 目	誤	正
本文 p. 348		
左段, 上から 6 行め	$2.0 \times 10^2 \pm 0.1 \times 10^2$ cc/min	$2.0 \times 10^3 \pm 0.1 \times 10^3$ cc/min