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HEAT OF IMMERSION OF SILICON NITRIDE

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ABSTRACT

Heat of immersion and contact angle were measured for α-Si_3N_4. The electrostatic field strength, which was determined to be 0.42×10^5 esu cm^{-2}, showed that the surface is much less polar than those of oxides. Slight increase of the heat of immersion in water with the increase of outgassing temperature is attributable to the rehydration of siloxane linkages which have been formed by dehydration of silanol groups on the surface. The heat of immersion in n-alkanes increased steeply with the number of carbon, n, from n=6 to 9, and became nearly constant for $n>9$, while in n-alkanols the heat began to rise at n=10 after the nearly constant values for n=4 to 8. The dispersion force contribution to the total surface free energy, γ_s^d, were estimated by contact angle and heat of immersion methods which have been well applied to the low energy surfaces, and found to be 25 mJ m^{-2} from contact angle and 129 mJ m^{-2} from the immersional heat in hexane.

INTRODUCTION

The nature of ceramic surfaces play an important role in various technological applications. There have been a number of investigations on the surface properties of oxides, but few dealt with non-oxides such as carbides, nitrides and sulfides, which have recently been regarded as strong candidates of engineering ceramic materials. In the present work, heat of immersion and contact angle were measured for α-silicon nitride. Since the result suggested that the polarity of the surface was very low, the average surface free energy has been estimated by the methods which have been successfully applied to many non-polar solids of relatively low surface energies such as polyethylene and teflon.

EXPERIMENTAL

Materials

Silicon nitride, α-Si_3N_4, which was prepared by thermal decomposition of silicon imide, was obtained from Ube Industries, Ltd. BET surface area was 12.8 m^2 g^{-1} and oxygen content was 1.5 wt.%. Organic liquids for immersion experiment and contact angle measurement were dried on the molecular sieves.

Measurements

A conduction type twin-microcalorimeter (Tokyo Riko MPC-111) was used for the measurement of heat of immersion. The samples (*ca.* 0.2 g) were outgassed in 1

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cm^3 glass ampoules at the specified temperatures for 24 hr and sealed under vacuum. The calorimeter was thermostated at 25^{0}C.

Usually contact angle is measured directly by contacting the liquid droplets with flat surfaces of solids. Since, in the present work, it was desired to know the surface properties of as-received sample powder, the contact angle measurement was made for powder sample by so-called ($h - \varepsilon$) method (ref. 1). The powder is compacted to a cake in a stainless steel mould by applying pressure of 500 kg cm^{-2} under a laboratory press. As Fig. 1 shows the cake is placed on a platform which can be adjusted to ensure the cake surface is horizontal. Liquid is applied dropwise to the center of the surface by a syringe. Initially the liquid penetrates into the cake. After saturation of pore with the liquid, the liquid will no longer penetrates and a stable drop is formed on the surface. The height, h, of the drop is measured by a travelling microscope. The contact angle(θ) can be calculated from

$$\cos\theta = 1 - \sqrt{\frac{Bh^2}{3(1-\varepsilon)(1-Bh^2/2)}} \quad , \qquad B=\rho g/2\gamma_l \tag{1}$$

where ρ is the density of the liquid, g the acceleration due to gravity, γ_l the surface tension of the liquid and ε the volume porosity of the cake. The porosity was calculated from the apparent density of the cake in mercury.

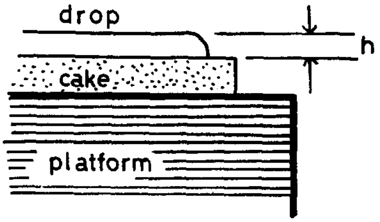

Fig. 1. Liquid drop formed on the cake surface.

RESULTS AND DISCUSSION

Electrostatic field of surface

The average strength of the electrostatic field of α-Si_3N_4 surface was estimated from the heats of immersion in the liquids with various dipole moments. According to Zettlemoyer's method (ref. 2), the samples were immersed in n-heptane, n-butanol, n-butyl chloride and n-nitropropane. In Fig. 2 the net energy of interaction calculated from the heat of immersion, ΔH_i, and the surface enthalpy of the liquid, ΔH_l, is plotted against the dipole moment, μ, of the immersing liquid. The electrostatic field strength, F, calculated from the slope of the straight line in Fig. 2 was found to be 0.42x10^5 esu cm^{-2}. This is comparable to that previously obtained for As_2S_3(F=0.29x10^5 esu cm^{-2}, ref. 3). The value is substantially lower than those of the oxides such as silica (Aerosil, F=1.1x10^5 esu cm^{-2}, ref. 4) and titania (rutile, F=2.7x10^5 esu cm^{-2}, ref. 2) and suggests that the surface is much less polar than those of the oxides.

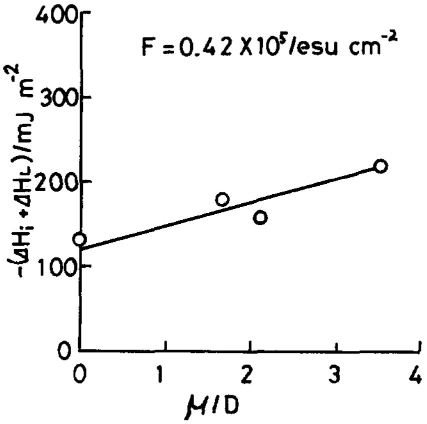

Fig. 2. Plot of heat of immersion *vs*. dipole moment, and F calculated from the slope of the line.

Heat of immersion in water

In Fig. 3 the observed heats of immersion in water are plotted against the outgassing temperature. Each sample has been outgassed for 24 hr at 100^0 intervals from 100^0 to 500^{0}C. The exothermic heat slightly increases with the increase

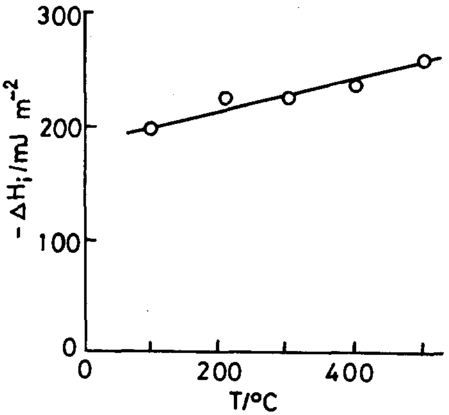

Fig. 3. Relation between heat of immersion in water and outgassing temperature.

of the outgassing temperature. A large portion of the oxygen contained in silicon nitride is known to be concentrated at the surface region probably forming siloxane linkages, Si-O-Si, which may be hydrolyzed by moisture in atmosphere to form silanol groups, Si-OH. Although the result shown in Fig. 3 is different from that of silica in the temperature dependence, which in many cases shows a maximum, the tendency to increase slightly with the outgassing temperature is attributable to the rehydration of siloxane linkage on the surface of oxygen-containing silicon nitride.

Heats of immersion in n-alkanes and n-alkanols

The immersion of the solids, whether they may be polar or not, in non-polar liquids, say n-alkane homologs, is expected to give similar values of the heat of immersion. It has been reported, in fact, that the heats of immersion of rutile in hexane, heptane and octane were close together (ref. 5). In Fig. 4 the heats of immersion in the homologs of n-alkane from hexane to hexadecane are plotted against the n (the number of carbon) in C_nH_{2n+2}. For n from 6 to 9 the heat increased steeply with n, after that it became nearly constant up to n=13.

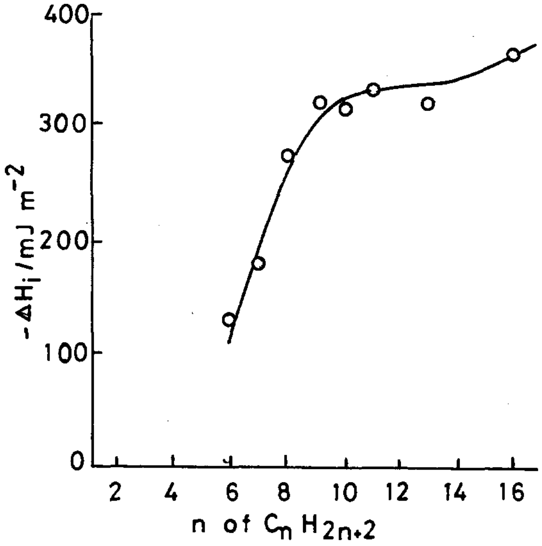

Fig. 4. Plot of heat of immersion *vs.* n in C_nH_{2n+2}.

In n-alkanols, on the contrary, the change of the heat of immersion was very slight for butanol (n=4) to octanol (n=8) as shown in Fig. 5. Since the dipole moments of the homologs of n-alkanols lie about 1.6 D, the heat of immersion was expected to be nearly independent of n. It was true for n=4 to 8, for $n>10$, however, the heat showed steep rise. The increase of the immersional heats in n-alkanes of $n>13$ and in alkanols of $n>10$ can be attributable to the effect similar

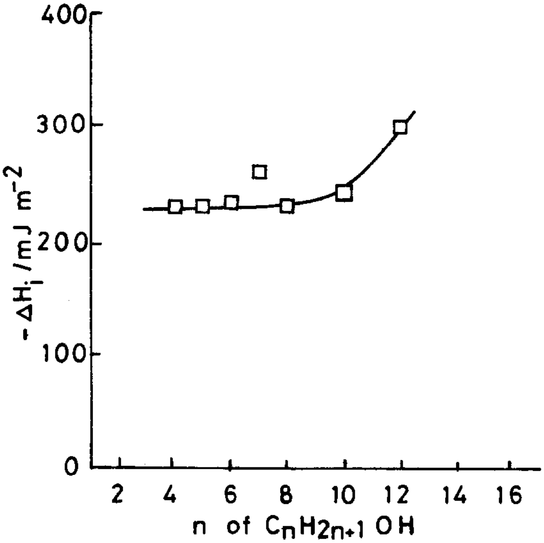

Fig. 5. Plot of heat of immersion *vs.* n in $C_nH_{2n+1}OH$.

to "structuring effect" observed by Clint *et al.* (ref. 6) in the case of immersion of non-porous graphite in n-alkanes and n-alkanols. We have had no interpretation yet for the abrupt increase of the heat of immersion observed in hexane to nonane in the present work.

Estimation of the surface free energy

Since, as described previously, the polarity of α-Si_3N_4 surface is very low, the attempt was made to estimate the surface free energy by the methods which have been applied well for the non-polar and low surface energy solids such as polyethylene and teflon. By taking the geometrical mean for the interfacial free energy (ref. 7) and neglecting the surface pressure for the liquids which contact with the solid surface with contact angle larger than 0°, we have the equation,

$$\gamma_l(1+\cos\theta)=2(\sqrt{\gamma_l^d\,\gamma_s^d}+\sqrt{\gamma_l^p\,\gamma_s^p}) \qquad (2)$$

where γ is surface free energy, the subscripts l and s refer to the quantities of the liquid and solid, and the superscripts d and p are used to designate the contribution of dispersion force and the other polar contribution, for example dipole-dipole interaction and hydrogen bond, to the surface free energy, respectively. Two unknowns, γ_s^d and γ_s^p, in eqn. (2) can be determined from the contact angles observed with two liquids of known γ_l^d and γ_l^p.

The contact angles were measured with water and methylene iodide, the results

TABLE 1

Surface free energy data and observed contact angles on $\alpha\text{-}Si_3N_4$.

Liquid	γ_l^d	γ_l^p	γ_l	$\theta_{obsd.}$
H_2O	23.4	48.8	72.0	27°
CH_2I_2	50.4	0	50.4	23°

are shown in Table 1. γ_s^d and γ_s^p determined from the observed contact angles by eqn. (2) are 25 mJ m^{-2} and 46 mJ m^{-2}, respectively.

The geometrical mean approximation also gives the following equation for the relation between dispersion force contribution and heat of immersion (ref. 7).

$$\Delta H_i^d = \gamma_l - 2\sqrt{\gamma_l^d \gamma_s^d} - T\left(\frac{d\gamma_l}{dT} - 2\sqrt{\gamma_s^d}\,\frac{d\gamma_l^d}{dT} - 2\sqrt{\gamma_l^d}\,\frac{d\gamma_s^d}{dT}\right) \qquad (3).$$

In the present case, γ_s^d was calculated from ΔH_i in hexane, in which the intermolecular attraction is entirely due to dispersion force. For $d\gamma_s^d/dT$ is very small and generally amounts to about 2% of the total heat of immersion (ref. 7), the last term in the parenthesis on the right hand side of eqn. (3) was neglected in the present calculation. The result was 129 mJ m^{-2}, which was fairly large compared with that obtained from the contact angles by eqn. (2). We can not conclude that which result is reasonable, at present.

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REFERENCES

1 P.M. Heertjes and N.W. Kossen, Powder Tech., 1 (1967) 33.
2 J.J. Chessick, A.C. Zettlemoyer, F.H. Healey and G.J. Young, Can. J. Chem., 33 (1955) 251.
3 M. Hattori and T. Ogasawara, Thermochim. Acta, 63 (1983) 51.
4 A.C. Zettlemoyer, J.J. Chessick and C.M. Hollabaugh, J. Phys. Chem., 62 (1958) 489.
5 A.C. Zettlemoyer, Ind. Eng. Chem., 57(2) (1965) 27.
6 J.H. Clint, J.S. Chunie, J.F. Goodman and J.R. Tate, Nature(London), 223 (1969) 51.
7 F.M. Fowkes, Ind. Eng. Chem., 56 (1964) 40.