Wetting of aqueous solutions of organic binder (PVA) on sapphire and fused quartz

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Wetting by PVA aqueous solution of sapphire and fused quartz was studied by measuring the contact angle of a sessile drop placed on them. At a given temperature, the contact angle increased with increasing concentration of solution up to 2% and became rather constant for further increase in concentration. The contact angle also increased with increasing temperature. At temperatures over 70° C, the contact angle for sapphire exceeded 90° for PVA aqueous solutions of concentration over 2%. The effects of temperature and concentration on wetting for fused quartz were similar to those found for sapphire. These results are discussed in terms of bulk thermodynamics.

1. Introduction

Wetting of ceramics by organic binder solution is believed to be important for the binder distribution in the binder-ceramic system [1-3]. Because binder distribution in binder–ceramic mixture affects forming and handling in ceramic processing, a full understanding of wetting is needed for the development of better ceramics. In the past, wetting of ceramics by molten metal has been studied [4-9], but wetting by organic binder solution is not well understood. The aim of this research was to clarify the wetting of ceramics by binder solution.

The two model ceramics chosen for examination were sapphire (single-crystal alumina) and fused quartz. The former represents a model for conventional oxide ceramics. The latter represents the oxidized surfaces of silicon carbide and silicon nitride. Polyvinyl alcohol (PVA) was selected as a model binder, because it is widely applied in ceramic processing and fully characterized material is easily available. Wetting was determined by measuring the contact angle for a sessile drop of binder solution placed on the horizontal surface of ceramics. Temperature and concentration dependences of wetting are studied. They should be directly related to the phenomena which occur during the drying process of the ceramic–binder mixture at high temperatures. The wetting on both materials was found to decrease with increasing binder concentration and temperature. Solution having a binder concentration over 2% was repelled by the alumina surface above 70° C. The significance of these findings is discussed in terms of bulk thermodynamics.

2. Materials and methods

Commercial PVA (Grade PA-05, Shin-Etsu Kagaku Kogyo Co., Niigata, Japan) was applied to prepare aqueous solutions of various concentrations (0.2 to 10%). For contact angle measurement, home-made equipment was used which allows measurement in the temperature region 25 to 80° C. Commercial polished sapphire and fused quartz were used for the substrates. To standardize the surface conditions, the substrate was soaked in 5% NaOH solution overnight, in concentrated nitric acid at 70 to 80° C for 2 h and washed with distilled water. After drying in air, the substrate was placed in a desiccator with activated alumina desiccant. For measurement of contact angle, the substrate was placed in the apparatus saturated with steam at the temperature of measurement for 30 min. A fixed amount of PVA aqueous solution (~0.01 ml) was dropped on the substrate, and the shape of the sessile drop was recorded with a camera through the glass-mounted window of the apparatus. To repeat the measurement, another drop was placed at a different position on the substrate. The contact angles were measured on the printed photographs, and ten measurements were averaged for each condition.

3. Results

Fig. 1 shows examples of sessile drops placed under different conditions. The shape of the drop varied significantly with temperature, concentration of solution, and substrate.

Fig. 2 shows the effects of temperature and concentration on the contact angle for PVA aqueous solution on sapphire. The contact angle for both distilled water and PVA solutions increased with increasing temperature, and also increased with increasing PVA concentration. Surprisingly the contact angle exceeded 90° for PVA aqueous solutions for concentrations over 2% at a temperature over 70° C. The concentrated solution tended not to wet the substrate at higher temperatures.

Fig. 3 shows the effect of concentration on the contact angle for PVA aqueous solution on sapphire. At a given temperature, the contact angle increased with increasing concentration of PVA aqueous solution,
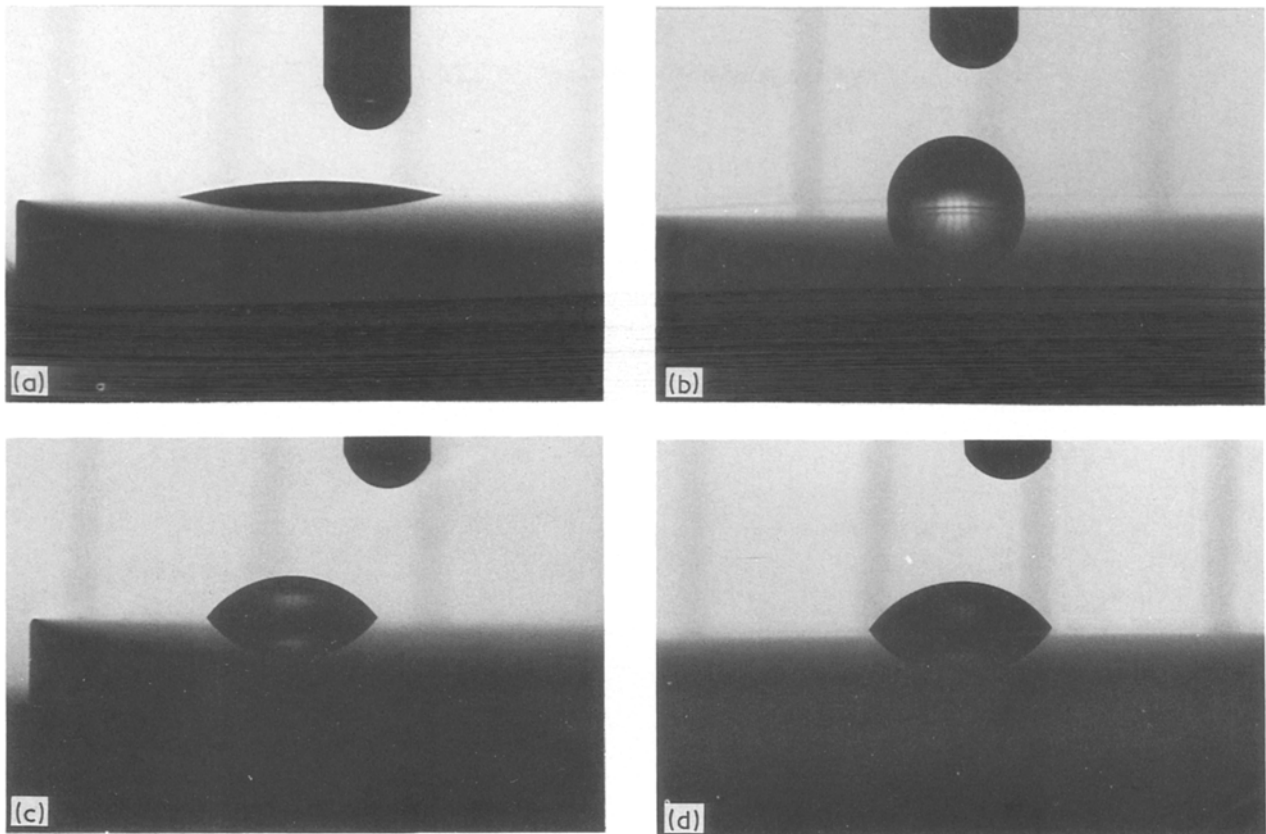
Figure 1 Shape of sessile drops of PVA aqueous solution, (a) 15° C, and (b) 70° C for 2% PVA aqueous solution on sapphire; (c) 0.2% PVA aqueous solution on sapphire at 70° C; (d) on fused quartz for 2% PVA aqueous solution at 70° C.

and became rather constant at a concentration over about 2%.

Fig. 4 shows the effects of temperature and concentration on the contact angle for PVA aqueous solution on fused quartz. The effects of temperature and concentration are similar to those found for sapphire. However, the contact angle on fused quartz is much smaller than that for sapphire, at a given temperature and concentration of solution. That is, the wetting of fused quartz by the PVA aqueous solution is better than that of sapphire.

4. Discussion

In the processing of ceramics, the raw powder is mixed into a slurry with the binder solution and sprayed into a flow of heated atmosphere to form granules. Binders mixed in this way have various roles in ceramics processing. They give granules a reasonable strength and stability of shape. The spherical granules can flow freely and can fill the pressing die homogeneously during the pressing process. The binders may also serve to give a proper strength in the pressed body. Other additives are frequently used to give proper characteristics in the binder–powder mixture. Homogeneous distribution of binder and other additives is strongly needed for the production of better ceramics.

Wetting of ceramics powder by binder solution must be very important in governing its distribution in granules. During the drying process at a high temperature, non-wetting solution mixed with powder must be segregated at some region, and inhomogeneous powder–binder mixture may result. A region rich in binder (poor in ceramic powder) may cause an area of low density in a sintered body. Low-density regions
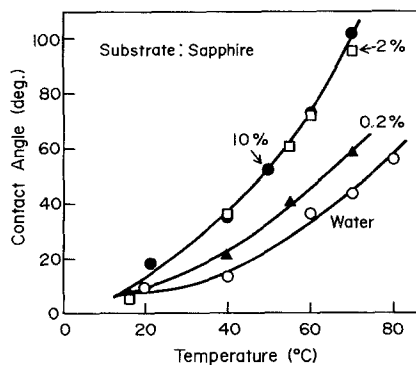

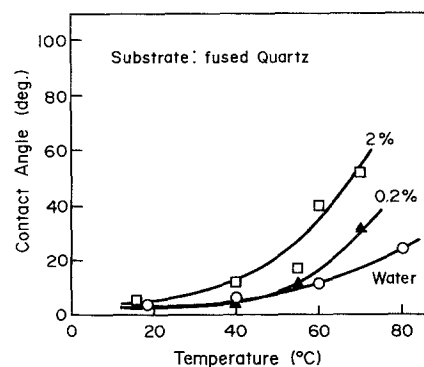*Figure 2* Effects of temperature and concentration on the contact angle for PVA aqueous solution on sapphire.

Figure 3 Effect of concentration on the contact angle for PVA aqueous solution on sapphire.
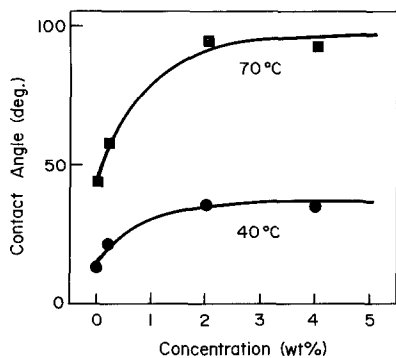
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Figure 4 Effects of temperature and concentration on the contact angle for PVA aqueous solution on fused quartz.

Figure 5 Free energy change, ΔG, as a function of temperature.

are known to behave as flaws and reduce the strength of the ceramics.

The wetting characteristics found in this study must be very important for understanding the behaviour of binder in the ceramic–binder system. Of particular importance is the temperature dependence of wetting. Because sprayed slurry is dried at approximately 100° C, reduced wetting at increased temperature may introduce inhomogeneities into the dried granule even for a system which has full wetting at lower temperatures. The result also shows that drying at lower temperature is favourable for a more homogeneous distribution of binder in granules. The addition of surface active agent may also be important, but the effect of temperature must also be examined before its application. More detailed examination giving the wetting–distribution relationship will be left for the subsequent study.

The contact angle at the solid–liquid interface is given by Young's equation

$$\cos \theta = (\Gamma_{SV} - \Gamma_{SL})/\Gamma_{LV} \qquad (1)$$

where Γ_{SV}, Γ_{LV} are, respectively, the surface energies of solid–vapour and liquid–vapour phases, Γ_{SL} the interfacial energy of solid–liquid phases and θ the contact angle. The surface energy of water vapour decreases from 72 to 63 erg cm^{-2} as the temperature increased from 25 to 80° C. Reliable values are absent for Γ_{SV} and Γ_{SL} for the present system. However, qualitative understanding is possible. Recalling that the origin of surface energy is the interrupted chemical bonding at the surface, and that the energy of chemical bonding in a solid bulk tends to decrease with increasing temperature [10], both solid–vapour and liquid–solid interfacial energies are also expected to decrease with increasing temperature. The reduced wetting with increasing temperature shows that the difference in solid–vapour and solid–liquid interfacial energy becomes less positive with increasing temperature, and becomes negative at about 70° C for PVA concentration above 2%.

Bulk thermodynamics seems to be helpful for the further discussion. The reaction of aluminium oxide and aluminium hydroxide is given by the following equation
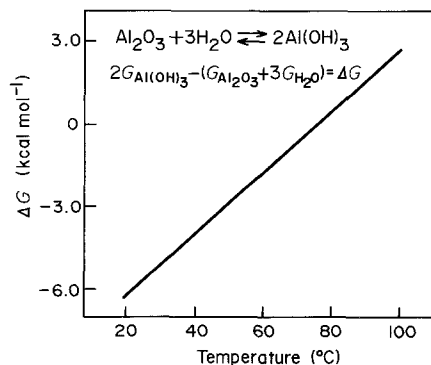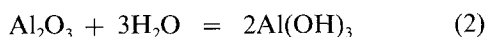
$$Al_2O_3 + 3H_2O = 2Al(OH)_3 \qquad (2)$$

The free energy change for this reaction, ΔG, is given in Equation 3.

$$2G_{Al(OH)_3} - (G_{Al_2O_3} + 3G_{H_2O}) = \Delta G \qquad (3)$$

where G is the Gibbs free energy for corresponding substances. The change in Gibbs free energy calculated from Equation 3 is shown in Fig. 5 as a function of temperature [11]. At temperatures below 80° C it was found to be negative, and positive at temperatures over 80° C. This means that aluminium oxide attracts water to form aluminium hydroxide at lower temperatures, and the surface tends to be covered with water. At higher temperatures, the free surface of aluminium oxide becomes more stable and the binder solution is repelled from the surface.

For discussing the wetting behaviour with changing concentrations of PVA, a detailed knowledge of the interfacial energies are required for both solution–vapour and solution–alumina interfaces. Toyoshima studied the wetting behaviour for PVA solution at room temperature and found similar results to this study [12]. The solution–vapour interfacial energy was found to be insensitive to the PVA concentration in the solution. Their argument given for the solution–substrate interfacial characteristics was basically the same as ours, but we give a more explicit explanation below.

The change of contact angle with concentration of PVA solution may be explained by assuming that the PVA molecules tend to be repelled from the alumina surface in the solution, and that they do not change the solution–vapour interfacial energy significantly. Under these assumptions, the number of PVA molecules at the solution–alumina interface is low at low PVA concentrations in the solution, and the wetting of the solution is approximately the same as that of distilled water. Complete depletion of PVA molecules from the interface region, however, enhances the free energy of the total system, and a small but increasing number of PVA molecules must be present at the interface region with increasing PVA concentration in the solution. The surface energy and, consequently, the wetting angle, increase with increasing PVA concentration. When the solution–alumina interface is completely covered with PVA molecules, further increase of the PVA concentration in the solution does not affect the interfacial energy. In this case, the wetting does not change further with PVA concentration.

The concentration above which the contact angle becomes constant was 1 to 3% in this and past studies. Naito *et al.* [13] reported the change of structure in PVA solution in this concentration region. The significance of molecular interaction may be studied in the subsequent study.

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