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### Publication Date

1979



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

Submitted to the American Ceramic Society

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January 1979

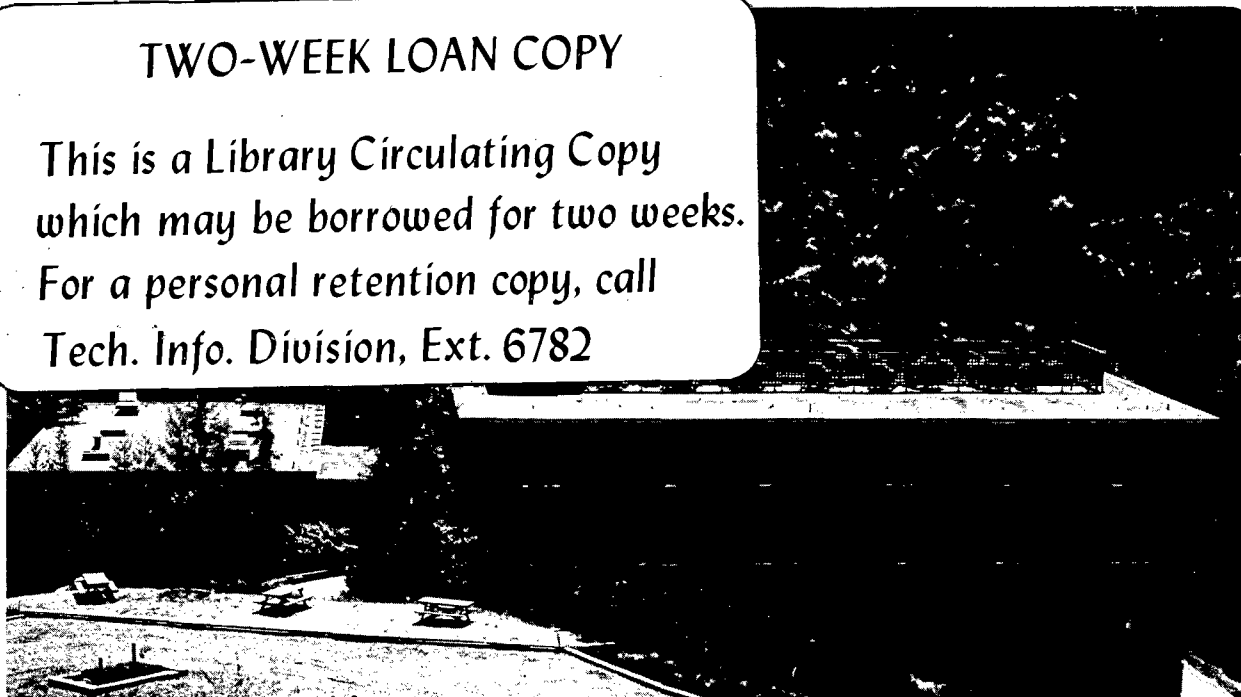
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## WETTING AND ADHERENCE OF Na-BORATE GLASS ON GOLD

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### INTRODUCTION

Previous work in this laboratory on the wetting behavior of sodium borate 'solder' glass (nominally 94%  $B_2O_3$  and 6%  $Na_2O^*$ ) on platinum has been reported.<sup>1</sup> It was found that the Pt surface easily adsorbed carbonaceous contaminants causing a reduction of its surface energy which affected the sessile drop experiments. It was also found that the glass readily adsorbed water vapor resulting in a reaction between the glass and Pt which caused spreading of the glass and development of adherence. The question arose as to whether this glass would behave similarly on gold. This report presents the results of the study.

### EXPERIMENTAL PROCEDURE

Gold plate of 99.95% purity<sup>†</sup> and 0.02 in. thickness was cut into 0.5 in. x 0.5 in. squares. The squares were polished through a set of dry polishing papers and given a final polish on a lap wheel with 0.3 micron  $\alpha$ -alumina powder. They were cleaned with an ultrasonic cleaner, degreased in acetone, rinsed with alcohol and distilled water, and stored in a desiccator before use.

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Based on thesis submitted by Stephen T. Tso for Master of Science in Materials Science, University of California at Berkeley, December 1976.

\* Obtained from Dow Chemical Co., Walnut Creek, CA.

† Obtained from Lawrence Livermore Laboratory.

The previously mentioned glass (composition given in Ref. 1) was used in this study. Since it usually contained a great deal of dissolved water, it was vacuum degassed ( $2 \times 10^{-6}$  torr) for about one day at  $900^{\circ}\text{C}$  in an alumina crucible until the glass ceased to bubble. Only the central portion of the degassed glass was stored in a desiccator until ready to use. From the original glass, about 3% sodium oxide boiled off while ~0.3% alumina diffused into the glass from the crucible during the process of vacuum degassing. Use of glass without degassing always resulted in bubbling during the sessile drop experiments.

Two set-ups were used for the sessile drop experiments. The first set-up contained a tantalum tube resistance heating element, which was described previously.<sup>2</sup> The total pressure in the chamber was about  $2 \times 10^{-6}$  torr. The second set-up consisted of a one-inch diameter fused silica tube, a portion of which was placed in the interior of a clam shell Kanthal resistance wire furnace.<sup>1</sup> This arrangement permitted experiments with atmosphere control without its exposure to the heating element.

The nitrogen gas used had a purity of 99.999%, The oxygen gas used was 99.6% pure; its major impurities were Argon (4000 ppm max.), nitrogen (500 ppm max.), and carbon dioxide (1.5 ppm). Water vapor was introduced into the furnace tube by aspiration. During the course of the experiments a liquid nitrogen cold trap was activated as required. Contact angles in both cases were measured at  $900^{\circ}\text{C}$  with an estimated accuracy of  $\pm 2^{\circ}$  by sighting with a telescope. Sufficient time (~6h) was taken to assure that steady state contact angles had been achieved.

## RESULTS AND DISCUSSION

Sessile drop experiments of the sodium borate glass on platinum indicated that without a cold trap carbon adsorption occurred on the platinum due to carbonaceous vapor backstreaming from the oil diffusion pump.<sup>1</sup> In order to determine whether the wetting behavior of the test glass on gold would indicate possible carbon contamination of the gold surface, specimens were treated as follows: (1) as received, (2) heat-treated in air at 900°C for 8 hrs, and (3) heat-treated in vacuum ( $10^{-8}$  atm) at 900°C immersed in carbon powder for 24 hrs. The observed contact angles in vacuum ( $10^{-8}$  atm) at 900°C with no cold trap decreased gradually but became constant at 46° after 3 hrs for all 3 metal specimens, and remained unchanged for an additional 10 hrs. This behavior was reproducible in the pressure range of  $10^{-8}$  atm to  $10^{-5}$  atm indicating that the gold surfaces had reached a constant structure irrespective of any initial differences that may have existed. In order to eliminate the possibility that all of the gold surfaces might have had carbon contamination due to carbonaceous vapor backstreaming from the oil diffusion pump, an experiment was repeated with an activated liquid nitrogen cold trap using a gold specimen that was heat treated in air. A contact angle of 46° was obtained indicating that the gold surface was inert to carbon adsorption from carbonaceous vapor.

At a pressure of 500 $\mu$ m Hg water vapor, bubbles were produced at the gold/glass interface at 900°C. The glass drop vaporized completely in less than 2 hrs. The evaporation rate in oxygen was  $2.8 \times 10^{-7}$  g/sec-cm<sup>2</sup> and in water vapor,  $1.8 \times 10^{-4}$  g/sec-cm<sup>2</sup>. The increased weight loss and bubbling suggests that the water vapor was absorbed by the glass and also

reacted with the glass. Additional evidence for this reaction was an unsteady drop with a contact angle showing a range of 39 to 60°. The lack of development of adherence suggested that the bubbling was due to a boiling phenomenon and not a reaction with the substrate with evolution of a gaseous reaction product.

At an ambient pressure of 1 atm nitrogen, the wetting behavior was found to be the same as that in vacuum. Steady state contact angles of 46° were again obtained. Using Young's equation and a value of 80 ergs/cm<sup>2</sup> for the glass<sup>3</sup>, ( $\gamma_{sv} - \gamma_{sl}$ ) is 56 ergs/cm<sup>2</sup>, or the surface energy of the substrate is reduced by the glass by this amount. Using the published value of 1370 ergs/cm<sup>2</sup> for gold<sup>4</sup>,  $\gamma_{sl}$  becomes 1314 ergs/cm<sup>2</sup>.

At ambient pressures greater than 15 $\mu$ m Hg oxygen the contact angle was 6°; at lower pressures, 46°. The relation between the steady state contact angle and the partial pressure of oxygen is shown in Fig. 1. It was also observed that in the oxygen atmospheres the glass drops tended to migrate until they reached the edge of the gold substrate. This phenomenon was not observed in vacuum, nitrogen or water vapor. As the glass drop drifted, the whole drop did not move as a unit but a film of glass was left behind the drop like a tail, which was so thin that it was difficult to detect. When the gold pieces were bent, the films fractured indicating the presence of chemical adherence. In the absence of chemical bonding the glass pops off cleanly on bending the metal piece. The fact that in oxygen a film of glass formed behind the moving glass drop that was contiguous with the drop indicates that its composition was different from the bulk glass since the glass would otherwise retain its drop shape. It is postulated that this film is approaching

saturation with gold oxide at the interface because of the appearance of good adherence. These quantities are too small and too restricted to be determined by present analytical tools. Deterioration of adherence occurred with prolonged heating and was attributed to diffusion of gold oxide into the bulk glass resulting in loss of saturation at the interface. The edge of the glass drop or film, however, still retained its adherence due to some diffusion of oxygen along the interface from the gold/glass/air periphery line.

The decrease of contact angle to  $6^\circ$  in oxygen atmospheres indicates that  $(\gamma_{sv} - \gamma_{sl})$  is  $80 \text{ ergs/cm}^2$  since oxygen has little effect on the surface energy of liquid glass.<sup>5</sup> Oxygen, however, chemisorbs on gold surfaces<sup>6</sup> and using a value of  $1210 \text{ ergs/cm}^2$  for  $\gamma_{sv}$  for gold in oxygen,<sup>4</sup>  $\gamma_{sl}$  becomes  $1130 \text{ ergs/cm}^2$ . The decrease of  $\gamma_{sl}$  by  $184 \text{ ergs/cm}^2$  on exposure to oxygen occurs with the development of chemical bonding. This deduction is consistent with previous findings<sup>7,8</sup> and with the theory that adherence occurs when the glass and metal at the interface are saturated with the substrate metal oxide.<sup>9</sup>

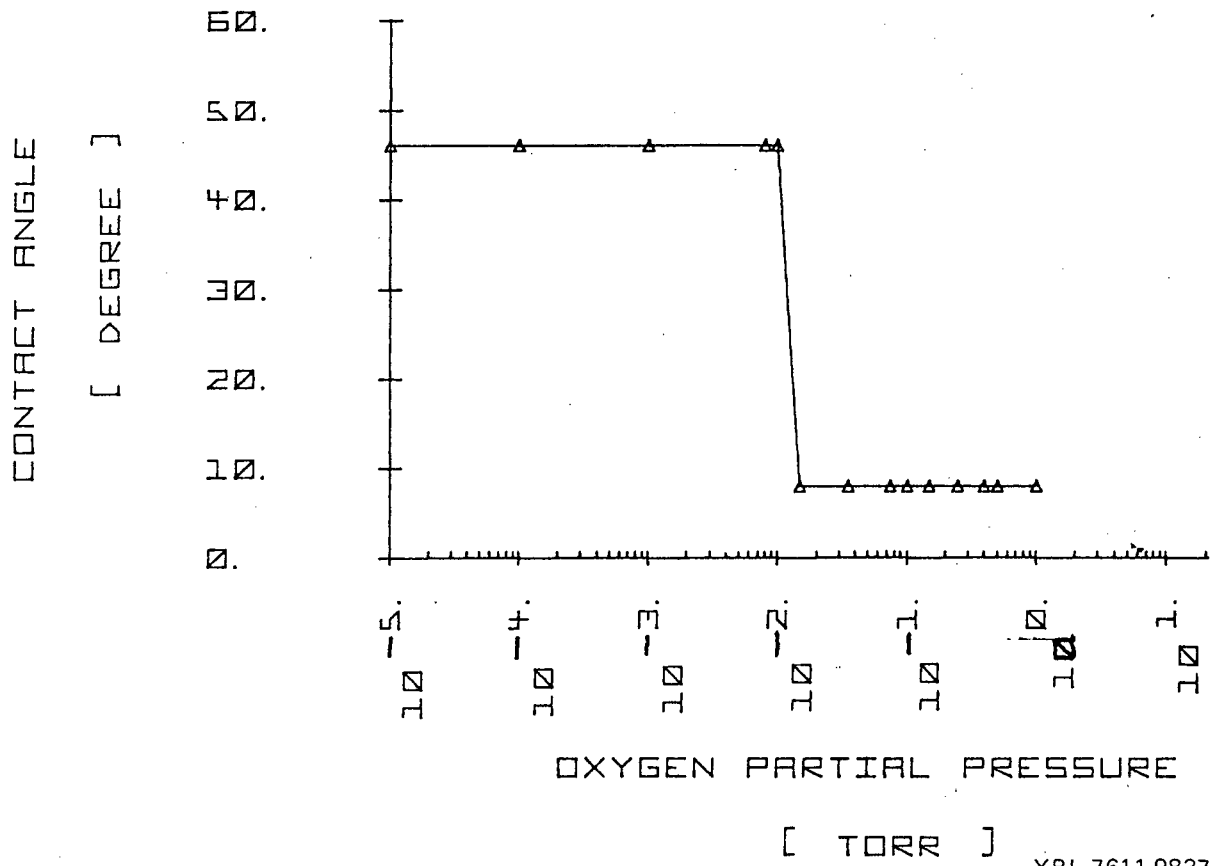


FIGURES

Fig. 1. Contact angle vs. oxygen pressure at 900°C for Na-borate glass on gold.

ACKNOWLEDGMENT

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.



XBL 7611-9837

Fig. 1

REFERENCES

1. G. A. Holmquist and Joseph A. Pask, "Effect of Carbon and Water on Wetting and Reactions of  $B_2O_3$ -Containing Glass on Platinum," J. Am. Ceram. Soc., 59, [9-10] 384-386 (1976).
2. J. J. Brennan and J. A. Pask, "Effect of Nature of Surfaces on Wetting of Sapphire by Liquid Aluminum," J. Am. Ceram. Soc., 51, [10] 569-573 (1968).
3. W. D. Kingery, Introduction to Ceramics, 2nd edition, John Wiley & Sons, Inc., p. 183, 1975.
4. Harry Udin, "Measurement of Solid: Gas and Solid: Liquid Interfacial Energies," in Metal Interfaces, American Society for Metals, Cleveland, Ohio, pp. 114-133, 1952.
5. N. M. Parikh, "Effect of Atmosphere on Surface Tension of Glass," (2) 40, J. Am. Ceram. Soc., 41 [1] 18-22 (1958).
6. M. A. Chesters and G. A. Somorjai, "The Chemisorption of Oxygen, Water and Selected Hydrocarbons on the (111) and Stepped Gold Surfaces," Surface Science 52, 21-28 (1975).
7. N. A. Shishakov, et al., "The Structure and Mechanism of the Formation of Oxide Films on Metals," Izd-Vo An SSSR, p. 63, 1959.
8. D. G. Moore and H. R. Thornton, "Effect of Oxygen on the Bonding of Gold on Fused Silica," J. Research National Bureau of Standards, 62, [3] 127 (1959).
9. Joseph A. Pask and Richard M. Fulrath, "Fundamentals of Glass-to-Metal Bonding: VIII. Nature of Wetting and Adherence," J. Am. Ceram. Soc., 45 [12] 592-596 (1962).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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