

# SURFACE PROPERTIES OF LIQUID METALS: BISMUTH, LEAD-BISMUTH, TIN

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## Summary

Dissolved oxygen was shown to have inappreciable surface activity in liquid bismuth up to 700 °C. Introduction of lead as a third solute in the liquid bismuth however increased the surface activity of oxygen. The solutes oxygen, sulphur, selenium, and tellurium showed the same order of surface activity in liquid tin as in liquid lead.

## I. INTRODUCTION

The preceding papers of this series have recorded the wetting behaviour of liquid metals such as lead (Bradhurst and Buchanan 1959*a*, 1959*b*), sodium and sodium-potassium mixtures (Bradhurst and Buchanan 1961*a*), and bismuth (Bradhurst and Buchanan 1961*b*) towards oxide surfaces. In general, pure liquid metals show marked non-wetting characteristics on all oxide surfaces up to quite high temperatures. On the other hand introduction of certain non-metallic solutes such as oxygen and the halogens may greatly improve the wetting even in quite low concentrations. Such surface active solutes must clearly accumulate at the surface of the liquid metal and in this way reduce its metallic character. In the present paper further studies are recorded on surface activity in bismuth, bismuth-lead mixtures, and tin.

## II. EXPERIMENTAL

The sessile-drop technique for measuring surface tensions and contact angles of the liquid on a solid surface has been described previously (Bradhurst and Buchanan 1959, 1961*a*).

Pure specimens of the metals to be investigated were obtained from the Metallurgy Department, University of Melbourne. Cylindrical pellets (3.5 × 6.5 mm) were prepared using a stainless steel punch and the weighed solutes were confined before melting in small holes drilled in the tops of the pellets. The lead-bismuth eutectic alloy was prepared in a graphite container in the evacuated furnace.

## III. RESULTS

### (a) Surface Activity of Oxygen in Liquid Bismuth

Weighed amounts of Bi<sub>2</sub>O<sub>3</sub> were added to molten bismuth and surface tension and contact angle on UO<sub>2</sub> determined (Table 1).

The concentrations of oxygen shown in column 1 are in fact in excess of the saturation value of 0.00695 mole % Bi<sub>2</sub>O<sub>3</sub> (Hansen 1958) and excess solid

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$\text{Bi}_2\text{O}_3$  was present on the surface of the drop throughout the experiment. Furthermore there was no evidence, on microscopic observation, of recrystallization of the oxide from the liquid metal on cooling the drop to room temperature.

TABLE 1  
SURFACE ACTIVITY OF OXYGEN IN MOLTEN BISMUTH

$\text{Bi}_2\text{O}_3$ (mole %)	Surface Tension at 700 °C (dyne $\text{cm}^{-1}$ )	Contact Angle (deg es)
0	$350 \pm 7$	$156 \pm 2$
0.063	$346 \pm 7$	$149 \pm 2$
0.318	$345 \pm 7$	$150 \pm 2$

TABLE 2  
SURFACE ACTIVITY OF OXYGEN IN LEAD-BISMUTH EUTECTIC

PbO (mole %)	Surface Tension at 700 °C (dyne $\text{cm}^{-1}$ )	Contact Angle (degrees)	Work of Adhesion (dyne $\text{cm}^{-1}$ )
0	$388 \pm 7$	152	45.4
0.369	$374 \pm 7$	130	133
0.786	$370 \pm 7$	120	18

TABLE 3  
COMPARISON OF SURFACE ACTIVITY IN TIN AND LEAD AT  
800 °C

Solute	Maximum Reduction in Surface Tension (% at 800 °C)	
	Sn	Pb
Oxygen .. ..	20.4	22.0
Sulphur .. ..	15.8	7.0
Selenium .. ..	12.0	5.0
Tellurium .. ..	2.0	2.5

(b) *The Lead-Bismuth Eutectic Mixture*

Oxygen, when dissolved in the lead-bismuth eutectic, displayed significant surface activity although the effects were rather less than for pure lead (Table 2). The largest value for the work of adhesion to  $\text{UO}_2$  corresponds approximately with that obtained for lead with oxygen as solute (198 dyne  $\text{cm}^{-1}$ ).

*(c) Surface Activity in Liquid Tin*

This metal was studied over the temperature range 250–800 °C and solutes used were oxygen, sulphur, selenium, and tellurium. Saturation concentration was achieved for the first two, which are the least soluble. The results at 800 °C are compared with a similar set obtained for liquid lead (Table 3).

## IV. DISCUSSION

The surface activity of oxygen in liquid bismuth is clearly very slight (Table 1) and in fact is scarcely significant. This may be associated with the quite low solubility of oxygen in liquid bismuth, although on the other hand experience in the case of lead (Bradhurst and Buchanan 1959a) indicated that the least soluble and least metallic of the solutes, oxygen, was the most surface active. In this connection introduction of lead into the bismuth (to give the eutectic composition) significantly improved the surface activity of oxygen as a third solute (Table 2). The contact angle on  $\text{UO}_2$  was decreased quite significantly although the surface tension was less definitely influenced. It is evident that the presence of lead as part of the liquid phase permits dissolved oxygen to accumulate in the surface either as oriented  $\text{PbO}$  molecules or ion pairs. Further studies on other solutes in bismuth (e.g. S, Se) would probably give some indication of the reason for the lack of surface activity (up to 700 °C) of oxygen in this metal.

Surface activity of the solutes oxygen, sulphur, selenium and tellurium in liquid tin show the same order of effectiveness as in liquid lead (Table 3). It is again evident that the important factor in determining whether a surface excess of solute will be established is the metallic character and compatibility of the solute with the liquid metal. In this connection the greater surface activity of sulphur and selenium in tin as compared with lead may be due to lower solubility and reduced compatibility of these elements with the metal.

The conclusions reached in this work may have consequences in interpreting liquid metal behaviour. Soft solder, for example, should flow and wet an oxidized metal surface more readily if the solder has already been subject to oxidizing conditions and contains a significant amount of dissolved oxygen. Naturally, flow will occur most readily on a clean non-oxidized solid metal surface. The role of a flux is probably to limit oxidation of the solid metal which is being soldered or welded. It could in certain circumstances provide non-metallic surface active solutes for the liquid metal and hence increase its ability to wet a partially oxidized solid metal surface.

## V. REFERENCES

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