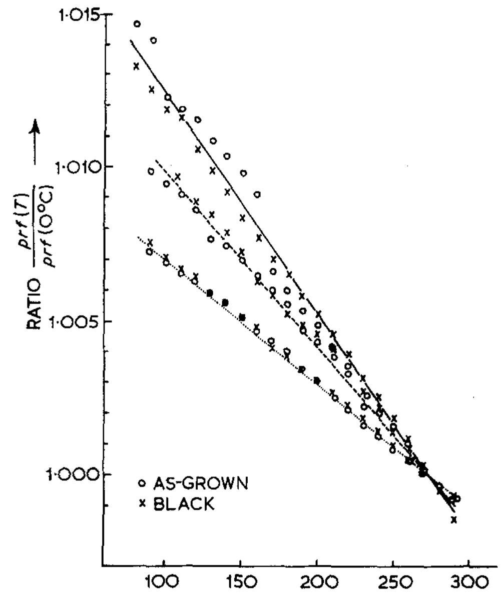

Figure 1 Comparison of temperature dependencies in as-grown and current-blackened 8 mol % YSZ single crystals. Key: open circles, as-grown; crosses, blackened Full line, shear mode with q along [001]. Chain line, shear mode with q along [1$\bar{1}$0]. Dotted line, longitudinal mode.

and is 12.0 for this solid solution. The Madelung attractive energy U_M has been calculated as -2945 kcal/mol and the repulsive energy U_n as 245 kcal/mol. Thus the total binding energy U_0 ($= U_M + U_n$) is -2700 kcal/mol. The elastic stiffness constants were also used to estimate the isotropic Young's modulus; the value obtained (2.1×10^{12} dyn cm^{-2}) can be compared with that (1.5×10^{12} dyn cm^{-2}) for polycrystalline sintered non-stabilised zirconia [5].

A comparison of results before and after blackening is made in fig. 1. It can be seen that the temperature dependencies are substantially the same. Within the experimental error the velocities are unaltered; the elastic constants in the as-grown and blackened states, and thus the lattice stabilities, are the same. This correlates with X-ray evidence [1] that the lattice parameter remains unaltered after blackening at low current densities. In the blackened crystal there was a marked deterioration of echo quality and some intermediate echoes also appeared: the blackened crystal shows the characteristics expected in an inhomogeneous material.

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J. M. FARLEY
J. S. THORP
J. S. ROSS
G. A. SAUNDERS
Department of Applied Physics and Electronics
University of Durham, UK

The Effect of Oxygen Pressure on the Liquid Silver-Alumina Interface

The effect of dissolved oxygen on the surface tension of molten silver has been studied by Eremenko and Naidich [1] who measured the dimensional change of a sessile drop of the metal supported on a ceramic substrate. The liquid-vapour surface tension (γ_{lv}) was calculated by the method of Bashforth and Adams [2]. Under vacuum, this surface tension is about 910 dyn cm^{-1} [1, 3], but with increasing oxygen solubility determined by increasing oxygen pressure, it decreases sharply and the drop spreads. At 10^{-3} atm, the surface tension is about 650 dyn cm^{-1}, but with further increase in oxygen pressures up to ~ 0.1 atm, it is reported to reach a roughly constant value of 600 dyn cm^{-1}.

Our studies by the above method indicate that there is still a detectable spreading of the drop with increasing pressure at oxygen pressures much greater than those above. Owing to changes in refractive index, and optical interference by gas turbulence, the results are assessed qualitatively.

The horizontal pressure vessel used was similar to that employed for previous work on the silver-oxygen system [4]. The furnace was wound with Nichrome and the bore of the furnace tube was 1.7 cm. The sapphire platform which supported the silver drop (wt 0.47 g) and which was mounted in the constant temperature zone, had been polished optically flat by 1 μm diamond paste. A glass plate closed the end of the furnace tube, and the drop was observed through it via a sapphire high-pressure window in the lid of the pressure vessel.

After evacuating to 10^{-3} atm, the vessel was flushed twice with the requisite gas and filled to the working pressure. The temperature was

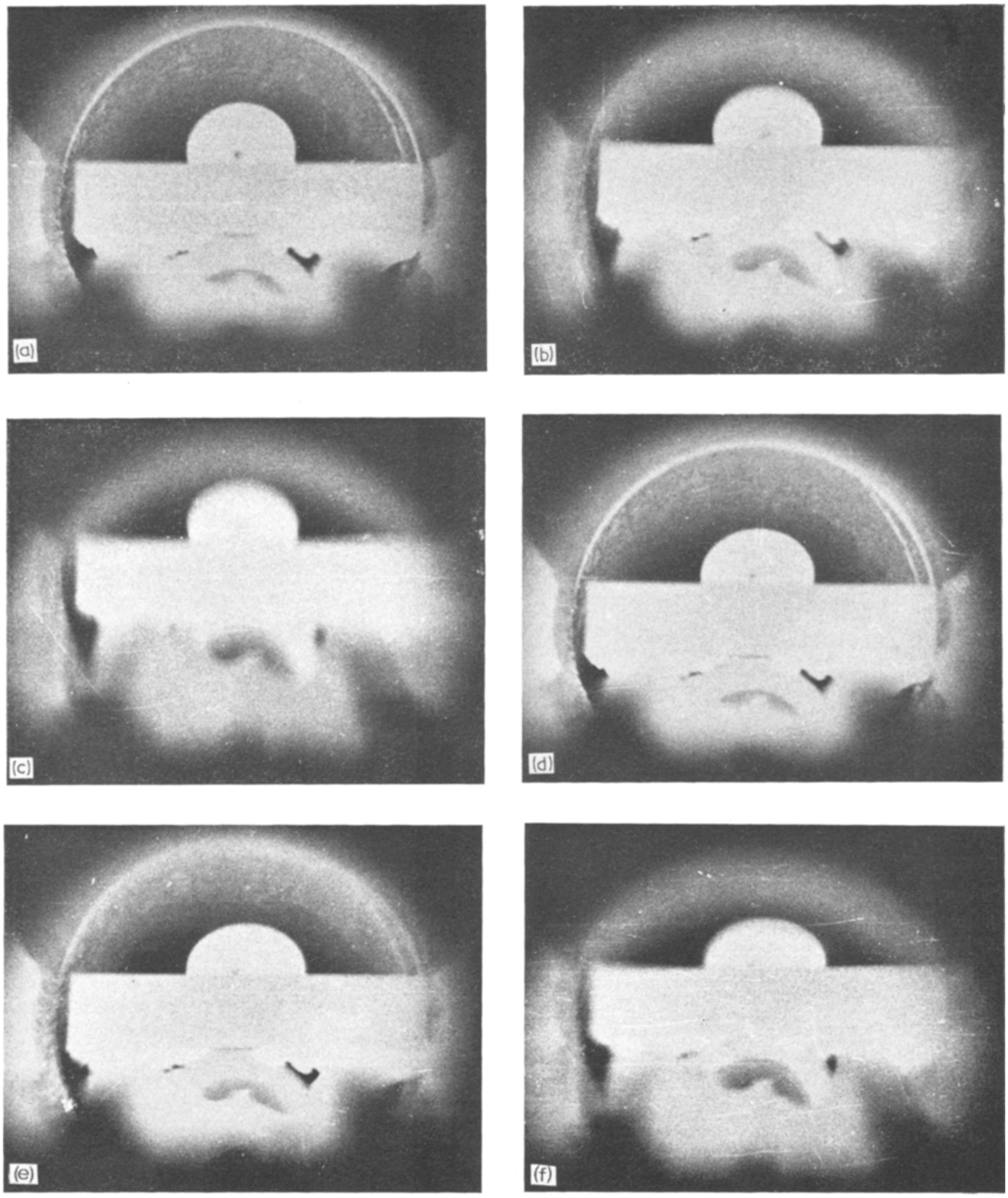

Figure 1 Sessile drop of liquid silver at 1000° C in different pressures of nitrogen and oxygen. (Magnification: ×3.) (*a*), (*b*) and (*c*) at nitrogen pressures of 1, 16, and 25 atm, respectively; (*d*), (*e*) and (*f*) at oxygen pressures of 1, 9, and 25 atm, respectively. For these oxygen pressures, the corresponding bulk Ag_2O contents are respectively, 2.1, 5.4, and 8.2 mol %.

raised to 1000°C and the sapphire platform brought to a horizontal position by means of levelling screws under the pressure vessel. A cathetometer was used in this operation. The most difficult part was positioning in the line of vision, and this could only be done by taking the position where the platform thickness appeared minimal. After allowing 30 min for the saturation solubility of oxygen to be reached, the drop was photographed. In some experiments, a quartz light pipe was placed in the furnace tube to reduce the effects of gas turbulence, but was discarded owing to the parallax distortion introduced. Extension of the equilibration period from 30 min to several hours did not observably affect the drop shape. Results are shown in fig. 1, the oxygen dissolved being expressed as Ag_2O content [4].

The nitrogen used contained about 10 ppm of oxygen, so that the drop shape in nitrogen will be affected by this impurity. As near as can be determined [2], the drop shape at 1 atm pressure of nitrogen (fig. 1a) corresponds to a value of γ_{lv} of about 800 dyn cm^{-1}. However, relative to this state, there is clearly a continuous spreading of the drop with increasing oxygen pressure up to 25 atm.

The form of the drop is determined by an equilibrium involving three surface energies γ_{lv}, γ_{sv} (solid-vapour) and γ_{ls} (liquid solid). These are related by the Young-Dupré equation,

$$\gamma_{sv} = \gamma_{lv} \operatorname{Cos} \theta + \gamma_{ls}$$

where θ is the contact angle.

Under the conditions here, the vapour pressure of silver will be its partial pressure in the gas phase. The effect of the hydrostatic pressure alone on the equilibrium cannot be determined, but is unlikely to be significant. This is shown by the fact that with nitrogen, which has a negligible solubility in silver, increase of pressure (fig. 1) has little effect. (Any detectable effect may well arise from dissolution of oxygen present as an impurity in the gas.)

We feel that the continued spreading of the drop and decrease in contact angle at high oxygen pressures is caused not so much by a variation in γ_{sv} or γ_{lv}, but by a decrease in γ_{ls} as a result of interaction of Ag_2O with the sapphire surface, the Ag_2O distributed between the solid and liquid, diminishing the interfacial energy.

In the study of the silver-oxygen system [4], no significant attack of the fused alumina crucibles was apparent. A slight interaction at the solid liquid interface will not measurably affect the bulk thermodynamic properties of the system, but it can alter the sensitive surface-tension phenomena. When the adherent silver drop was removed from the sapphire by nitric acid at the end of the oxygen experiments, the contact area was seen to be opaque, indicating that some interfacial reaction had taken place.

Chaklader *et al.* [5] dissolved large amounts of CuO in liquid copper and observed considerable spreading of the sessile drop on sapphire at 1230°C. At 72 wt % of added CuO, the contact angle was only 21°. They consider that Cu_2O at the interface reacts with the alumina to form $CuAlO_2$, which diminishes the interfacial energy; the presence of the last compound was confirmed by X-ray examination.

Whether the formation of an analogous surface complex, $AgAlO_2$ plays a part in decreasing the interfacial energy of the present system, cannot be determined; to obtain such a compound in isolatable form would require very high oxygen pressures. It is most likely that the Ag_2O is accommodated at the sapphire surface in solid solution.

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B. E. KNOX
E. H. BAKER
Nuffield Research Group in
Extraction Metallurgy
Imperial College
London, UK