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Effect of oxygen on the wettability of sapphire by liquid palladium

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The surface tension of liquid palladium and the contact angle between liquid palladium and sapphire have been measured at 1833 K as a function of oxygen pressure by the sessile drop method. Oxygen acted as a surface-active element on the surface of liquid palladium and at the interface between liquid palladium and sapphire, resulting in the decrease of the surface tension and the contact angle. The work of adhesion calculated from their values increased with increasing oxygen pressure, and had a constant value above 400 Pa. The maximum excess concentration of oxygen was estimated to be 7.3×10^{-6} mol m^{-2} for the surface and 6.9×10^{-6} mol m^{-2} for the interface.

1. Introduction

Oxygen has a strong effect in lowering interfacial tensions between liquid metals and solid oxides, and causes an increase in the wettability of the oxides by the metals, as is verified in the liquid iron–alumina system [1]. In bonding a metal to a ceramics material, therefore, the oxygen content in the metal or oxygen pressure in the working atmosphere is an important factor in controlling the wettability of the ceramic by the metal. However, the effect of oxygen on the surface and interfacial properties in liquid metal–solid oxide systems has been only quantitatively investigated for a few systems, namely Fe–Al_2O_3 [1, 2], Co–Al_2O_3 [3], Ni–Al_2O_3 [4], Ni–MgO [5], Cu–Al_2O_3 [6, 7], Ag–Al_2O_3 [8], Ag–SiO_2 [8, 9] and Pb–UO_2 [10]. Although, many more systems should be examined in order to clarify the behaviour of oxygen at the metal–ceramic interface, it is very difficult to control exactly the oxygen contents in most metals in equilibrium with a gas phase with the exceptions of the above metals and palladium due to their low solubilities of oxygen.

Palladium is widely used as an electrode, lead and a resistive material for bonding to ceramics in electronic devices, such as ceramic capacitors and hybrid integrated circuits. However, palladium–ceramic bonding has been scarcely studied [11, 12]. No study of the wetting behaviour in the palladium–oxygen–ceramic systems could be found in the literature by the current authors.

In the present study, the surface tensions of liquid palladium and the contact angles between palladium and sapphire have been measured as a function of oxygen pressure using the sessile drop method. From these measured values, the maximum excess concentrations of oxygen adsorbed on the surface and at the interface have been evaluated.

2. Experimental

2.1. Materials

Sapphire (single crystal alumina) disks 20 mm in diameter and 1 mm thick (Kyocera) were used as substrates for the sessile drop method. The surfaces of the disks were optically flat and coincident with the $(01\bar{1}2)$ plane. High-purity palladium wires 1 mm in diameter (Johnson Matthey Chemicals) were used, which contained the following impurities: Au 3 ppm; Fe 1 ppm; Ca, Mg and Si < 1 ppm. The wire was coiled to a spiral of about 1.4 g so that it could be placed on a sapphire substrate.

2.2. Experimental set-up

The experimental set-up comprises a furnace, an optical system, a gas circuit and an oxygen gauge, as is shown in Fig. 1. The horizontal tube furnace was specifically made for measuring the surface tension of a metal and the contact angle between the metal and a ceramic material at temperatures near 1900 K using the sessile drop method, as shown in Fig. 2. The temperature was measured with a Pt–30% Rh/Pt–6% Rh thermocouple, and was controlled within ± 0.5 K at a given temperature. Photographs of the sessile drop were taken with the camera which was equipped with a 200-mm telephoto lens by a bellow 250 mm long. The oxygen pressure in the furnace was controlled with Ar–O_2 mixtures. The mixtures were prepared from Ar, Ar–0.1% O_2 and O_2 gases using the flow controllers. The oxygen pressure of a mixture flowing out of the furnace was monitored with a zirconia oxygen gauge operated at 973 K, which consisted of a ZrO_2–8 mol % Y_2O_3 electrolyte tube with Pt-paste electrodes on both the inner and outer sides of the tube in a non-inductive wound furnace.

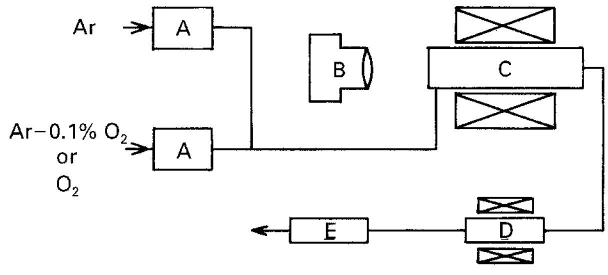

Figure 1 Experimental set-up: (A) flow controller, (B) optical system, (C) furnace, (D) oxygen gauge and (E) flow meter.

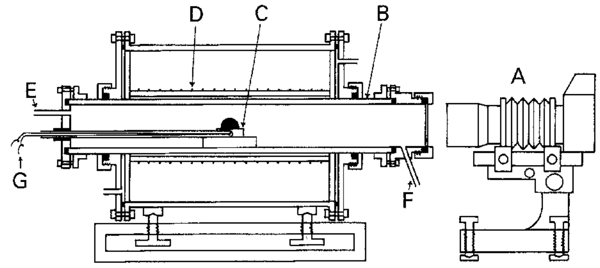

Figure 2 Apparatus for surface tension and contact angle measurements: (A) optical system, (B) alumina tube, (C) sapphire substrate, (D) molybdenum heater, (E) gas outlet, (F) gas inlet and (G) Pt–30% Rh/Pt–6% Rh thermocouple.

2.3. Procedure

A sapphire substrate was placed on the alumina pedestal in a uniform-temperature area, and then was accurately levelled. A palladium sample was placed on the substrate, and then Ar gas was flowed into the furnace at a rate of $200\ \mathrm{cm^3\,min^{-1}}$. After the oxygen pressure of the atmosphere in the furnace was checked with the oxygen gauge, the sample was heated to the experimental temperature, 1833 K. For pure palladium, the surface tension and contact angle were measured in the Ar gas. For palladium–oxygen alloys, after the temperature reached 1833 K, the Ar gas was replaced by an Ar–O_2 mixture with a given oxygen pressure. It is well known that a slight amount of oxygen leaking into a measuring system from the surroundings influences the oxygen pressure of an inert gas–oxygen mixture with a low oxygen pressure because of its poor buffer capacity against oxygen. This results in a significant flow rate dependence of the oxygen pressure in the system [13]. This indicates that, at low oxygen pressures, the oxygen pressures near the sample cannot be easily determined by the oxygen gauge which is measuring the gas at the outlet of the furnace. In the present study, the oxygen pressure measured at the oxygen gauge strongly depended on the flow rate at low oxygen pressures, below 0.01 Pa, but showed little dependence above 0.5 Pa at higher flow rates than $200\ \mathrm{cm^3\,min^{-1}}$. For palladium–oxygen alloys, therefore, measurements were carried out at oxygen pressures above 0.5 Pa and at a flow rate of $200\ \mathrm{cm^3\,min^{-1}}$.

Photographs of a drop were taken at 3 min intervals for 21 min, after a stable oxygen pressure was indicated by the oxygen gauge. Coordinates on the drop surface were read on the film. Surface tension and contact angle values were calculated from the coordinates by the Maze and Burnet method [14]. Density values required for the calculation were derived from the specific volumes of liquid palladium, $9.53 \times 10^{-5} + 1.15 \times 10^{-8}(T - T_m)$ $[\mathrm{m^3\,kg^{-1}}]$ [15], where T_m is the melting temperature of palladium, 1825 K, and T is the experimental temperature.

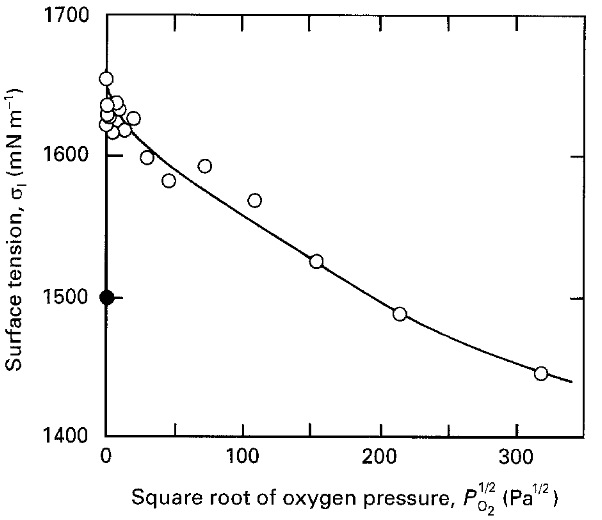

Figure 3 Surface tension of palladium as a function of the square root of oxygen pressure at 1833 K. Open circles data taken in present study at 1833 K, closed circle data of Allen at 1825 K [16].

3. Results

3.1. Surface tensions of palladium–oxygen alloys

The surface tensions of the palladium–oxygen alloys were measured in Ar–O_2 mixtures at 1833 K. The surface tensions are plotted in Fig. 3 as a function of the square root of oxygen pressure, which, according to the Sievert law, is proportional to the oxygen content. The surface tension of palladium decreased from $1655\ \mathrm{mN\,m^{-1}}$ in pure Ar as the oxygen pressure increased and reached a value of $1448\ \mathrm{mN\,m^{-1}}$ in pure oxygen.

Allen [16] obtained a value of $1500\ \mathrm{mN\,m^{-1}}$ for pure palladium at the melting temperature 1825 K using the pendant drop method. This value is approximately $150\ \mathrm{mN\,m^{-1}}$ lower than that obtained in the present study. The maximum amount of impurities in the sample used in his study was 0.2 mass %, and thus his low value of the surface tension is probably due to surface-active elements in the impurities.

3.2. Contact angles and work of adhesion values between palladium–oxygen alloys and sapphire

The contact angle is a direct measure of the wettability of a solid by a liquid. The contact angles between palladium–oxygen alloys and sapphire at 1833 K are shown in Fig. 4. The contact angle was 127.0° in pure Ar. This value is higher than the value 120° for polycrystalline alumina reported by Chatain et al. [17].

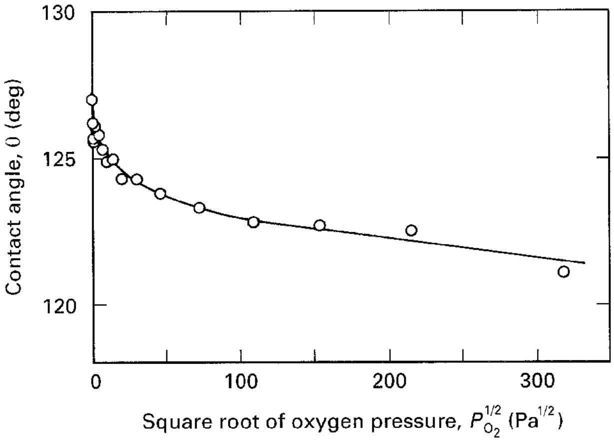

Figure 4 Contact angle between palladium and sapphire as a function of the square root of oxygen pressure at 1833 K.

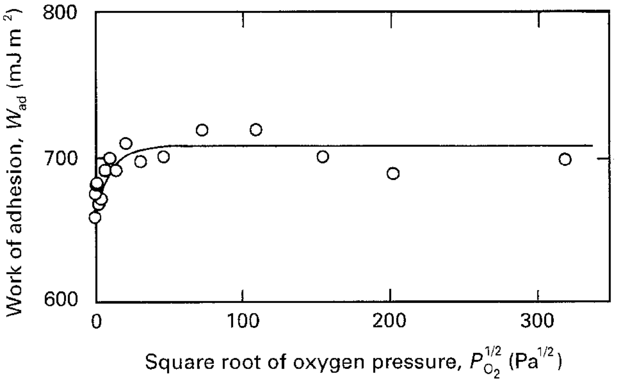

Figure 5 Work of adhesion between palladium and sapphire as a function of the square root of oxygen pressure at 1833 K.

The contact angle gradually decreased with increasing oxygen pressure, and had a value of 121.1° in oxygen.

The work of adhesion, which is the work required to separate a unit area of the interface into the two original surfaces is represented by the equation,

$$W_{ad} = \sigma_s + \sigma_l - \sigma_i \tag{1}$$

where σ_s and σ_l are the surface energies (= surface tensions) of sapphire and palladium and σ_i the interfacial energy (= interfacial tension) between them. Using the Young equation,

$$\sigma_i = \sigma_s - \sigma_l \cos\theta \tag{2}$$

where θ is the contact angle, Equation 1 becomes

$$W_{ad} = \sigma_l(1 + \cos\theta) \tag{3}$$

and hence, the work of adhesion can be obtained from the surface tension and contact angle values. The values of the work of adhesion between palladium–oxygen alloys and sapphire are shown in Fig. 5. The value for pure palladium is 659 mJ m^{-2} in the present study which is lower than data previously reported in the literature [17, 18] in which the work of adhesion differed widely, being between 691 and 1115 mJ m^{-2}. With increasing oxygen pressure, the work of adhesion increased and reached a constant value of 705 mJ m^{-2} at oxygen pressures above 400 Pa.

4. Discussion

4.1. Adsorption of oxygen on the surface of palladium

As is shown in Fig. 4, oxygen acts as a surface-active element. The excess surface concentration of adsorbed oxygen, Γ, can be estimated by the Gibbs adsorption equation,

$$\Gamma = -\frac{1}{RT}\frac{d\sigma_s}{d\ln X_O} \tag{4}$$

where R is the gas constant and X_O the oxygen content. Taking account of the Sievert law, $X_O = kP_{O_2}^{1/2}$, Equation 4 becomes

$$\Gamma = -\frac{2}{RT}\frac{d\sigma_s}{d\ln P_{O_2}} \tag{5}$$

Fig. 6 shows the surface tension as a function of ln P_{O_2}. The surface tension decreases sharply and linearly at high oxygen pressures above 1.2×10^4 Pa. This suggests that, above this pressure, the palladium surface was saturated with adsorbed oxygen. Therefore, the slope gives the maximum value of Γ, 7.3×10^{-6} mol m^{-2}. The maximum excess surface concentrations of oxygen for metals so far reported in the literature decreased approximately in the order Fe, Co, Ni > Cu, Ag > Pb, Sn [8, 19, 20]. The value obtained for palladium in the present study is relatively close to that obtained for Cu and Ag.

From the maximum excess surface concentration, the average area occupied by one oxygen atom, A, can be calculated. Using the relation $A = 1/(N\Gamma)$, where N is Avogadros' number, the value of 0.23 nm^2 is obtained. Taking into account that the average surface area of a palladium atom calculated from its specific volume [15] is 0.0657 nm^2, an oxygen atom should be adsorbed onto 3.5 atoms of palladium.

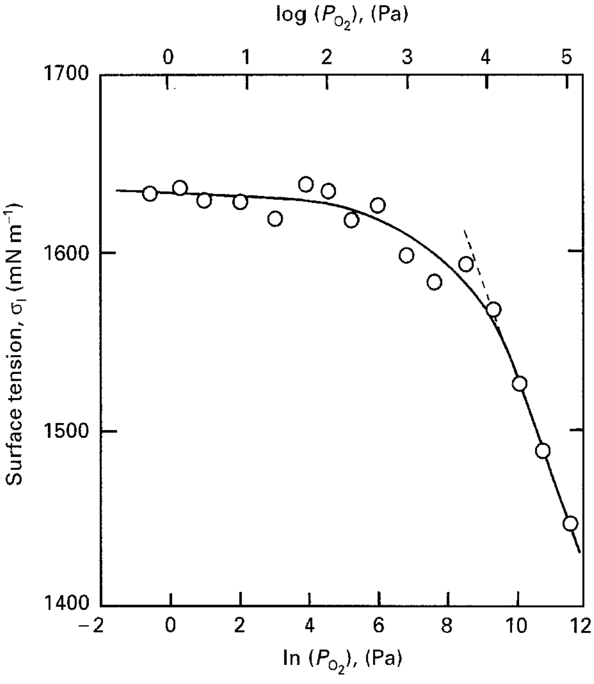

Figure 6 Surface tension of palladium as a function of the logarithm of oxygen pressure at 1883 K.

4.2. Adsorption of oxygen at the interface between palladium and sapphire

The interfacial tension between palladium and sapphire, σ_i, is represented by Equation 2. Since the surface tension of sapphire is considered to be unaffected by oxygen pressure, the excess concentration of oxygen at the interface is given by the equation,

$$\Gamma = \frac{2}{RT}\frac{d(\sigma_1 \cos\theta)}{d \ln P_{O_2}} \tag{6}$$

Fig. 7 shows $\sigma_1 \cos\theta$ as a function of $\ln P_{O_2}$. The maximum value of Γ at the interface is 6.9×10^{-6} mol m^{-2}, although it is not clear from this figure whether the interface between palladium and sapphire was fully saturated with adsorbed oxygen at the highest oxygen pressure 0.101 MPa (1 atm). This value is a little smaller than that obtained for the interface between liquid copper and sapphire [7]. As is shown in Fig. 5, the work of adhesion reached a constant value at an oxygen pressure of 400 Pa, but the interface is not yet saturated with oxygen. A similar result is reported in the liquid copper–oxygen–sapphire system [7].

4.3. Reaction between palladium and sapphire

In Fe–O–Al_2O_3 [1, 2], Co–O–Al_2O_3 [3], Ni–O–Al_2O_3 [4], Cu–O–Al_2O_3 [5] and Ag–O–SiO_2 [9] systems, double oxides as reaction products were observed at their interfaces at high oxygen contents or pressures. In the Ni–O–MgO system [5], the reaction zone was composed of the solid solution $(MgO)_{1-x}(NiO)_x$ which was formed even at very low oxygen pressures. These results are consistent with the following thermochemical conclusion: in the metal M–oxygen–oxide MeO system, a reaction zone composed of the double oxide nMO·mMeO phase, e.g., NiO·Al_2O_3, cannot be formed at lower pressures than the partial pressure of oxygen in equilibrium with the M, MeO and nMO·mMeO by the reaction,

$$n\mathrm{M} + m\mathrm{MeO} + n/2\mathrm{O}_2 = n\mathrm{MO}\cdot m\mathrm{MeO} \tag{7}$$

since the variance of freedom of the system is 1; however, a reaction zone composed of the solid solution of the MO and the MeO, e.g. $(MgO)_{1-x}(NiO)_x$, can be formed at any low oxygen pressure by the reaction,

$$x\mathrm{M} + (1-x)\mathrm{MeO} + x2\mathrm{O}_2 = (\mathrm{MeO})_{1-x}(\mathrm{MO})_x \tag{8}$$

since the variance of the freedom is 2 [21]. As is shown in Fig. 8, no reaction zone was observed in pure oxygen in the present study. In addition no reaction zones were found at the interfaces between solid palladium and alumina adhered in air or oxygen at high temperatures [11, 12, 22]. These facts indicate that alumina has no or only a very low solubility of palladium oxide and that compounds of palladium oxide and alumina would be formed at the interface at much higher oxygen pressures than 0.101 MPa (1 atm).

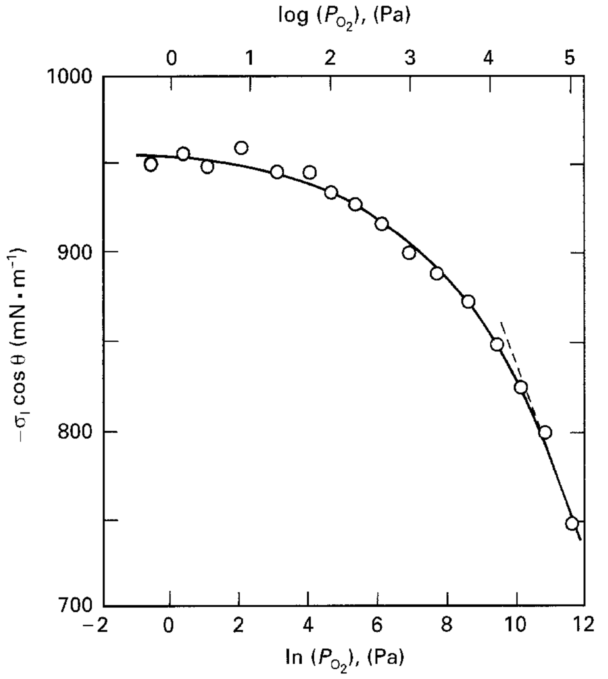

Figure 7 $\sigma_1 \cos\theta$ as a function of the logarithm of oxygen pressure at 1833 K.

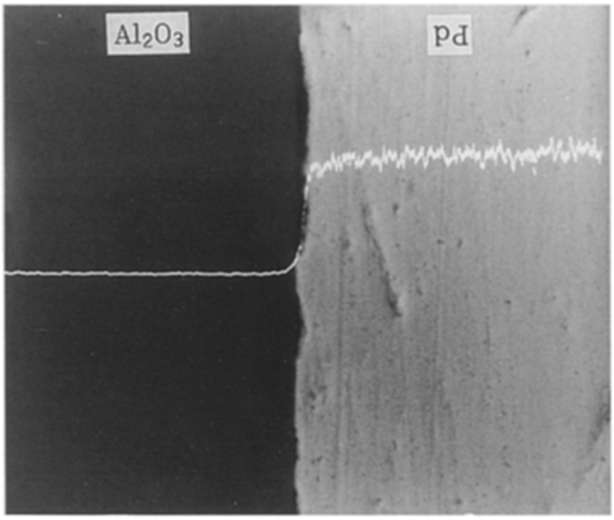

Figure 8 SEM photograph of the interface between palladium and sapphire after the measurement at 1833 K in pure oxygen. The line profile in the figure shows the L_α-ray intensity of palladium.

5. Conclusion

The surface tension of liquid palladium and the contact angle between liquid palladium and sapphire were measured at 1833 K in Ar and in Ar–O_2 mixtures with oxygen pressures of 0.5–0.101 MPa. The surface tension and the contact angle decreased from 1655 mN m^{-1} and 127.0° in pure Ar with increasing oxygen pressure and reached values of 1448 mN m^{-1} and 121.1° in pure oxygen. The oxygen was fully adsorbed onto the palladium surface at oxygen pressures above 1.2×10^4 Pa, and at the interface between palladium and sapphire at pressures much higher than this pressure. The maximum excess concentration of oxygen was estimated to be 7.3×10^{-6} mol m^{-2} for the surface and 6.9×10^{-6} mol m^{-2} for the interface. The work of adhesion increased with increasing oxygen pressure, and reached a constant value of

705 mJ m^{-2} at oxygen pressures above 400 Pa. At this pressure, the interface was not saturated with adsorbed oxygen. At the interfaces between palladium and sapphire after cooling, no reaction zone was found even at the highest oxygen pressure used in this study of 0.101 MPa.

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