JOURNAL OF MATERIALS SCIENCE LETTERS 5 (1986) 549–551

Influence of oxygen partial pressure on the wetting behaviour in the system Al/Al_2O_3

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The wetting of a ceramic material by a metallic melt is of importance in many technical applications, e.g. in the preparation of composites. The wettability of Al_2O_3 single crystals and polycrystalline material by molten aluminium has been investigated by many authors with the sessile-drop method in the temperature range 660 to 1350° C [1–8]. The results obtained show significant differences (Fig. 1), especially at temperatures below 1000° C, which are probably caused by different experimental conditions of the various investigations. Brennan and Pask [4] suspected that the characteristic sudden decrease of the contact angle at a specific temperature, as observed by many authors, is connected with the presence of an oxide layer on the metal surface. Therefore the influence of different oxygen partial pressures on the wetting behaviour has been investigated in this work.

Aluminium metal with a purity of 99.99% has been obtained from VAW Bonn, the main impurities were 0.002 mol % Si, 0.001 mol % Fe and 0.001 mol % Cu. Small cylinders with a diameter of 3.3 mm and a height of 3.2 mm (0.073 ± 0.0015 g) were fabricated from stock material by using aluminium oxide cutting tools and a diamond wheel. After ultrasonic cleaning in ethanol they were electropolished (36 V, 14 sec) before each experimental run in an electrolyte (700 ml methanol, 200 ml perchloric acid and 100 ml butylglycol). The electropolished samples were cleaned in ethanol, etched in 10% NaOH solution (35° C) for 3 min and in 2% HF-solution for 3 min and washed with water and ethanol again.

The aluminium oxide substrates were polished single-crystal materials (H. Djevahirdjian, S. A. Switzerland) of 13 mm diameter and 2 mm thickness with a surface roughness $R_a < 0.01\,\mu m$. They had been fabricated by the Verneuil process and had an orientation of the c-axis of 90 ± 5° vertical to the sample surface. Main impurities were 100 p.p.m. Si, 120 p.p.m. Mg and 110 p.p.m. Fe. In Fig. 2 the experimental apparatus is shown. It consists of a closed metal crucible 13.3 mm diameter and 30 mm high with a wall thickness of 0.5 mm, which is localized inside the high-temperature furnace of the Mettler Thermoanalyzer TA 1. The crucible contains the sample of aluminium metal upon the alumina substrate. Different oxygen partial pressures can be established if different metals are used as a crucible material. In this case the oxygen partial pressure depends on the oxygen equilibrium pressure above the metal–metal oxide system. Crucibles were made from steel (ST 34) copper, tantalum and zirconium metal; the whole system was purged for 1 h with argon ($O_2 \leqslant 0.1$ v.p.m., $H_2O \leqslant 0.5$ v.p.m.) before the start of each experimental run. The crucible was heated to 700° C with a linear heating rate of $10°\,C\,min^{-1}$. The temperature was kept constant for 2 h and then the furnace was cooled down with a linear cooling rate of $10°\,C\,min^{-1}$; the contact angle was determined after cooling.

In Fig. 3 the dependence of the wetting angle on the oxygen partial pressure is shown for a temperature of 700° C and a total pressure of 1 bar argon. The temperature of 700° C has been chosen, since the extent of

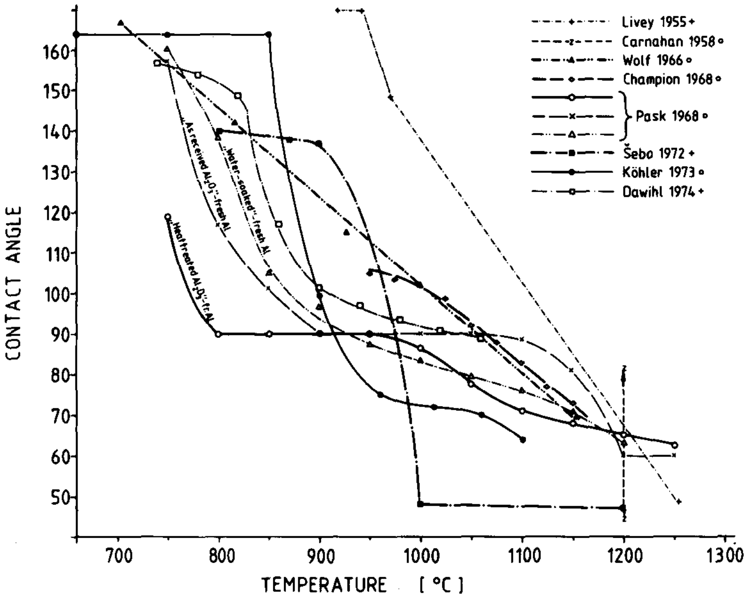

Figure 1 Contact angle in the system Al–Al_2O_3. Sessile drop experiments, vacuum. +, polycrystalline Al_2O_3; ○, single crystal Al_2O_3.

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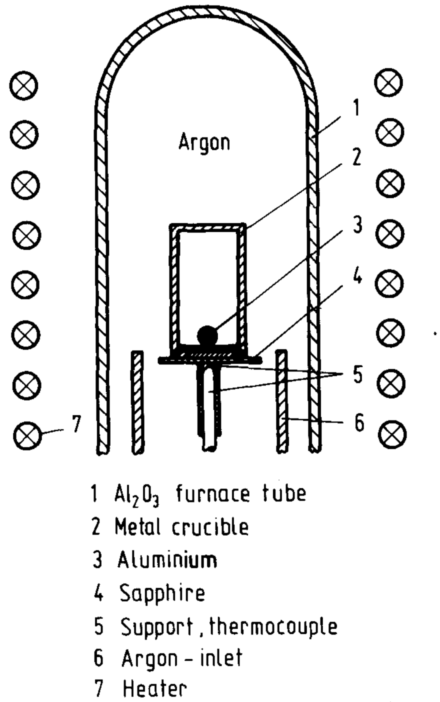

Figure 2 Experimental apparatus for experiments under different oxygen partial pressures.

the reaction between the molten aluminium and the solid aluminium oxide is very small at this temperature. At an oxygen pressure of 3.8×10^{-11} bar (Cu/Cu_2O) the oxide layer is so strong that no molten sphere could be formed (Fig. 4); at a partial pressure of 4.5×10^{-22} bar (Fe/FeO) the wetting angle is 162°, at 10^{-35} bar 110° and at 5×10^{-49} bar (Zr/ZrO_2) an angle of 90° is obtained. The equilibrium oxgyen partial pressure in the system Al/Al_2O_3 is 1×10^{-49} bar at 700° C, ZrO_2 and Al_2O_3 show almost the same stability at this temperature.

Since the solubility of oxygen in aluminium is extremely low [5, 9] different oxygen partial pressures in a sessile drop experiment will influence primarily the oxide layer thickness on the surface of the aluminium metal. At high oxygen pressures the oxide layer will prevent the formation of the equilibrium shape of the metal droplet because of the mechanical strength of the oxide skin. This effect will occur especially if the oxide layer covers the whole surface and exceeds a certain thickness. Sometimes thin layers disrupt at temperatures between 850 and 900° C and a sudden decrease in the wetting angle occurs (Fig. 1); this effect could be observed in some of our other experiments [10], where no additional oxygen getter was present as has been reported also by Brennan and Pask [4]. Very thin aluminium oxide layers on the metal samples have probably only a small influence since they can be deformed. It can be expected that even in the experiments performed in the zirconium crucible the aluminium samples were not completely free of oxide for the following reasons:

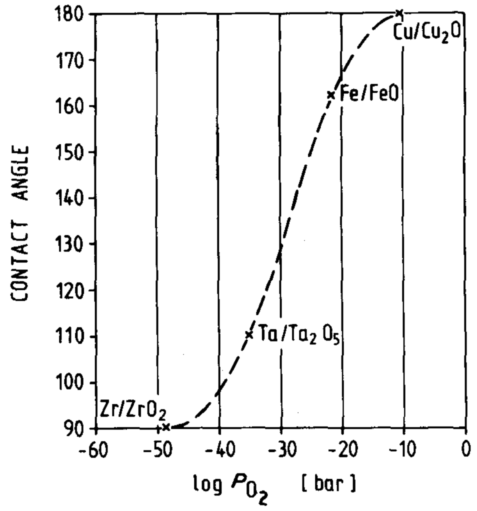

Figure 3 Contact angle and oxygen partial pressure (700° C, 2 h).

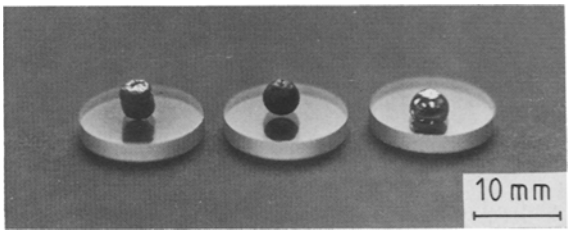

Figure 4 Aluminium droplets on sapphire after wetting experiments at 700° C under various partial pressures of oxygen (total pressure 1 bar argon). Left, $p_{O_2} = 10^{-11}$ bar; centre, $p_{O_2} = 10^{-22}$ bar; right, $p_{O_2} = 10^{-35}$ bar.

1. A thin (1 to 2 nm) oxide layer is always present on the surface of the aluminium metal sample because of the exposure to air.
2. The G_T^0 values for the metal–metal oxide equilibria are so similar that it is not possible to decide which oxide is more stable because of the uncertainty in the thermodynamic data [11].
3. It is not known if the equilibrium partial pressures have been obtained during the experiments; therefore the results shown in Fig. 3 should be seen relative to each other when the quantiative interpretation is concerned.

The results demonstrate that an oxygen partial pressure of $\approx 10^{-13}$ bar is the limit for the formation of a droplet by the liquid aluminium. Below 10^{-13} bar the wetting angle seems to be proportional to the logarithm of the oxygen partial pressure. Very low values for the wetting angle are obtained if a strong oxygen getter such as zirconium is present in the system.

The influence of different oxygen partial pressures on the shape of the sessile drop has been investigated at 700° C. Under the experimental conditions an oxide layer on the surface of the aluminium metal at an oxygen partial pressure of 3.8×10^{-11} bar prevented the formation of a spherical droplet completely. At very low oxygen partial pressures in the region of 10^{-49} bar the wetting angle at 700° C was as low as 90°.

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Received 5 November
and accepted 25 November 1985