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Wetting of Aluminum Oxide by Liquid Aluminum

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SUMMARY

The wetting of aluminum oxide by liquid aluminum can be improved considerably by a change of the interfacial energy between the oxide and the metal. The presence of an extremely thin carbon layer at the interface between the oxide and the metal results in a significant decrease of the contact angle.

1. INTRODUCTION

The wetting of aluminum oxide by liquid aluminum has been investigated by several authors using the sessile drop method.[1–8] In general, wetting does not occur below a temperature of 950°C, regardless of whether single crystal or polycrystalline material has been used. At 950°C a slight interaction between the metal and the oxide can already be observed; this is undesirable during the preparation of a fiber reinforced material as it could result in a weakening of the composite. Therefore, experiments with the aim of improving the wettability of the aluminum oxide are of interest. The influence of different parameters on the wetting behavior, e.g. changes in the composition of the metal, the oxide or the gas phase, or variations of the interface between the metal and the oxide, has been investigated extensively by John.[9] Some results of this work are reported below.

2. MATERIAL AND EXPERIMENTAL TECHNIQUES

2.1. Material

Small cylinders of aluminum (99·99%) with a diameter of 3·3 mm and a height of 3·2 mm were used. The samples were machined from aluminum

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rods by using aluminum oxide cutting tools and a diamond wheel. After ultrasonic cleaning in ethanol they were electropolished (36 V, 14 s) in an electrolyte (700 ml methanol, 200 ml perchloric acid, 100 ml butylglycol). The electropolished samples were cleaned in ethanol, etched in a 10% sodium hydroxide solution (35°C) for 3 min, in a 2% hydrofluoric acid solution for 3 min and then washed with water and ethanol.

The aluminum oxide substrates were of polished single crystal material (H. Djevahirdian, SA, Switzerland) of 13 mm diameter and 2 mm thickness, with a purity of 99·99% (main impurities: 100 ppm Si, 120 ppm Mg, 110 ppm Fe) and a surface roughness of $Ra \leq 0{\cdot}01\ \mu m$. They had been fabricated by the Verneuil process and had an orientation of the *c*-axis of 30 ± 10° from an axis perpendicular to the sample surface.

2.2. Sessile drop apparatus

For the wetting experiments an ultra-high vacuum system (1 μPa) was used. A tantalum heater (inner diameter 25 mm, total length 86 mm) surrounded by tantalum and molybdenum radiation shields was located in a water-cooled stainless steel chamber, which had two windows for the passage of a light beam. In the center of the heater an aluminum oxide plate (99·7% Al_2O_3), parallel to the optical axis, served as a support for the oxide substrate and the metal sample. An optical bench was located on both sides of the vacuum chamber. On one side a xenon high pressure lamp was fixed to the optical bench and illuminated the sample with a light beam 15 mm in diameter. On the opposite side a camera (6 × 6 cm) was attached and pictures could be taken during the various wetting stages. Temperatures inside the tantalum heater were controlled with W 3% Re/W 25% Re thermocouples. Programmed heating and cooling cycles were used in the experiments.

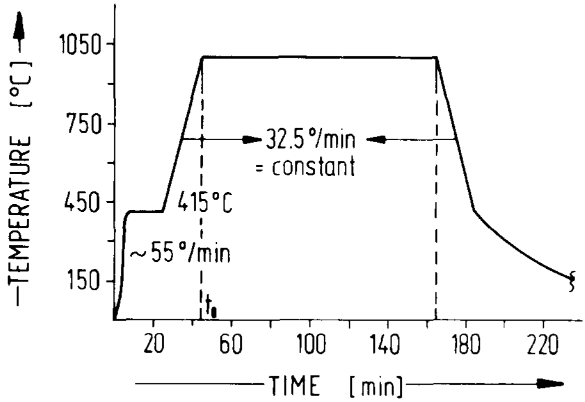

Fig. 1. Heating schedule.

2.3. Experimental technique

The single crystal substrate and the aluminum metal sample were positioned on top of the sample holder with a small manipulator. After pumping down the system to 40 μPa the wetting experiments were carried out according to the heating schedule shown in Fig. 1. The shape of the aluminum droplet was photographed periodically.

The contact angle was determined according to the procedure published by Bartlett and Hall.[10] A critical evaluation of all experimental errors showed that the contact angle could be determined with an accuracy of ±3% in the range between $40° \le \varphi \le 140°$.

RESULTS AND DISCUSSION

The time dependence of the contact angle at different temperatures is shown in Fig. 2. Each point of the curve is the median value from three experiments. At each temperature, with the exception of 1150°C, a rather steep decrease in the contact angle can be observed during the first few minutes. This steep decrease has been described in the literature as 'physical wetting' which starts after the sample has transformed completely into the liquid state. After about 15 min the change in the contact angle becomes smaller and remains constant.

At 700°C the change of the contact angle with time is extremely small,

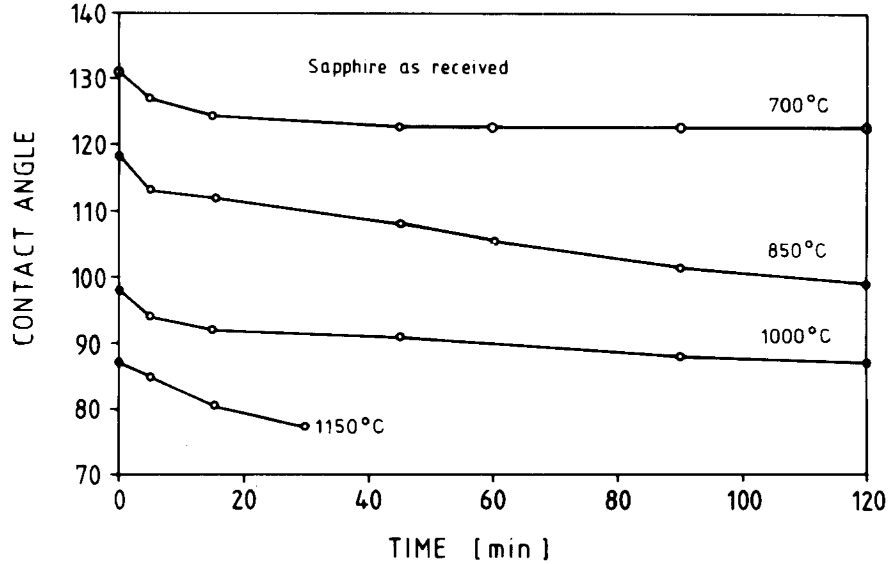

Fig. 2. Time dependence of wetting angle.

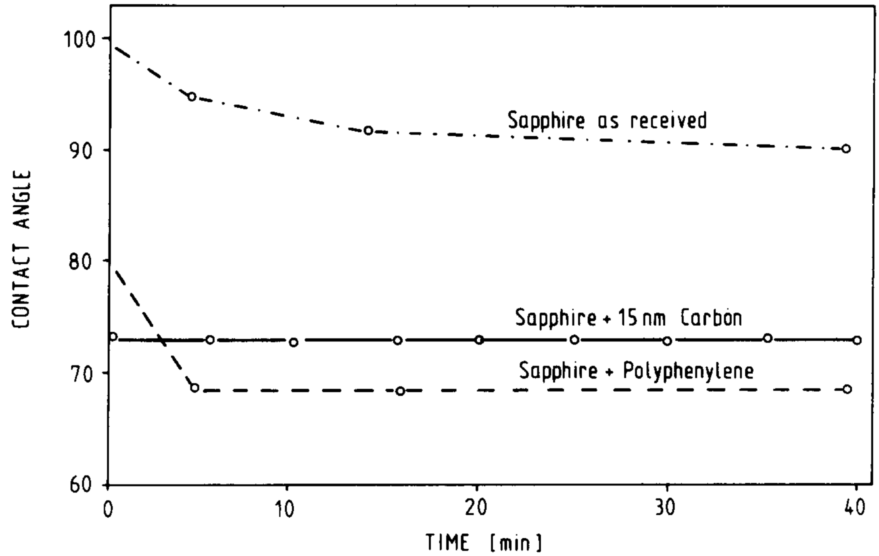

Fig. 3. Time dependence of wetting angle for an as-received sample and for two samples with a thin carbon layer on the surface (1000°C).

but at 1150°C it is significant. It is influenced by an interfacial reaction between the aluminum metal and the oxide, with the formation of suboxides at the low oxygen partial pressure inside the tantalum heater. At 1150°C strong vaporization of the aluminum metal, which limits the duration of the experiment to 30 min, may have an additional influence. Under the experimental conditions the contact angle drops below 90° at a temperature of 1000°C and wetting occurs. During the attempt to improve the wetting behavior of the oxide by the molten metal it could be observed by mass spectrometric analysis of the gas composition in the system that in some experiments an improved wetting behavior was associated with an increased concentration of hydrocarbons, carbon monoxide and carbon dioxide.

This observation led to a series of experiments where the surface of the aluminum oxide was intentionally contaminated with carbon. In Fig. 3 the change of the contact angle with time is shown for an as-received sample and for two samples with a thin carbon layer on the surface. In one case a 15 nm thick layer of carbon had been sputtered onto the substrate surface. The second sample had been treated with a 10% solution of polyphenylene in benzene, dried and used in this condition for the wetting experiment. During the heating-up period the polyphenylene is decomposed; the maximum weight loss occurs between 400 and 700°C, and the residual carbon content is 85·8 m/o. A marked reduction in the contact angle can be observed in the case of both carbon-coated samples.

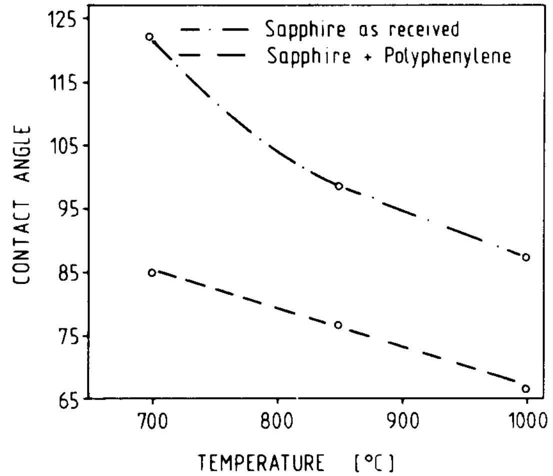

Fig. 4. Wetting angle after 120 min with and without carbon layers at different temperatures.

In Fig. 4 the contact angle at different temperatures is shown for single crystal aluminum oxide (sapphire) with and without a thin carbon layer made from polyphenylene.

It is possible to obtain a contact angle below 90° even at a temperature of 700°C in the case of the coated samples. The difference in the contact angle between the treated and untreated materials is about 20–30° for the whole temperature range.

The improvement in the wettability can be explained by the reaction between aluminum and carbon. Possible reaction products are aluminum carbide or oxycarbides (e.g. Al_2OC or Al_4O_4C). The presence of very small crystals could be observed at the interface between the oxide and the metal.

4. CONCLUSION

The wetting of aluminum oxide by molten aluminum can be achieved at a temperature as low as 700°C, if the surface of the aluminum oxide is first coated with a thin layer of carbon.

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