Applications of a High Temperature Sessile Drop Device

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Abstract. The wettability of a liquid metal on a solid surface is of great technological interest for the industry (soldering, brazing, infiltration) as well as for fundamental research (diffusion, chemical reaction, intermetallic phases). The characterization of wetting is done by measuring the contact angle at the triple line of the liquid on the solid. A High Temperature Sessile Drop Device (HTSDD) was constructed and several applications were tested: (i) a wettability study of a copper-based brazing alloy (Cu-ABA®) on TiNₓ coatings with different stoichiometries. The data derived from the HTSDD show that the reduction of the nitrogen content in the TiN coating reduces the time for reaching the final contact angle. Also for substoichiometric TiC a similar behaviour is predicted in literature. (ii) The liquid surface energy of molten metals can be estimated from the curvature of flattened droplets due to the influence of gravity. Two models were used for the calculation of the liquid surface energy of different liquid metals. (iii) From the droplet radius vs. time curves it is possible to distinguish between two different reactive wetting regimes – the diffusion and the reaction controlled reactive wetting. The beginning of this research topic will be discussed.

1. Introduction

Wettability studies are of great interest for industry and fundamental research. Metallic spreading is intrinsic to many industrial processes like soldering, brazing and thin film processing. Wetting properties are also needed to describe the liquid-state processing of composites, e.g. the infiltration of fiber preforms by liquid metals.

To study different wetting phenomena a High Temperature Sessile Drop Device (HTSDD) which is able to measure the contact angle of a liquid metal on a solid substrate up to temperatures of approx. 1100 °C was planned and constructed. The technical description of the device is given elsewhere [1]. In the sessile drop configuration the liquid metal forms a droplet on a solid substrate and the curvature of the drop is imaged optically.

2. Applications of the High Temperature Sessile Drop Device

The applications and the use of a sessile drop device can be extremely diverse. A good overview is given in [2]. Three different possibilities of using the HTSDD have been tested and are presented here: a wettability study of TiNₓ coatings of different stoichiometries, the measurement of the liquid surface energy of molten metals and the identification of different reactive wetting regimes.
2.1. Wetting of substoichiometric TiN\textsubscript{x}

Substoichiometric TiN\textsubscript{x} films are possible candidates for wetting promoting thin films in ITER (International Thermonuclear Experimental Reactor) relevant parts (e.g. divertor), where the brazing of Carbon Fiber-reinforced Carbon (CFC) onto the heat sink should be improved. Literature gives evidence that the wetting is dependent on the stoichiometry of the coating [2, 3].

The TiN\textsubscript{x} films were coated by reactive sputtering in a Physical Vapour Deposition (PVD) – chamber with a pure Ti target under different nitrogen flows, adjusted by a mass flow controller. The sputter parameters were: base pressure 10\textsuperscript{-5} Pa, working gas Ar with a flow of 8,1 sccm (approx. 0,2 Pa), nitrogen flows between 1,2 and 0,6 sccm and a D.C. power of 200 W.

First sputtering parameters were adjusted to those yielding stoichiometric TiN [4, 5]. Then the nitrogen content was gradually decreased and film deposition was started. The stoichiometry of the films was checked by Rutherford Backscattering (RBS).

The wetting experiments were done with the commercial active brazing alloy CuABA\textsuperscript{®} (Wesgo Ceramics, Germany, 92,75 wt% Cu, 3 wt% Si, 2 wt% Al and 2,25 wt% Ti) on different substrates: pure glassy carbon (GC, Sigradur\textsuperscript{®}G from HTW GmbH, Germany), GC with 100 nm Ti and GC with 100 nm TiN\textsubscript{x} of different stoichiometry. The results are shown in figure 1.

![Contact Angle of CuABA on different samples](image)

Figure 1. Contact angle study of brazing alloy (CuABA\textsuperscript{®}) on different substrates. A decrease in the contact angle vs. time is visible for all samples and the final contact angle is for all samples about 10°. It is evident that by reducing the nitrogen content of the TiN\textsubscript{x} coating, the time for reaching the final contact angle decreases (faster wetting). For the stoichiometry see the legend in the figure.

Here the contact angle evolution is plotted vs. the time of the wetting experiment. The final contact angle is for all samples in the range of approx. 10° but the time for wetting differs in the samples. The wetting on the pure GC takes the longest time (about twice the time than for the GC with Ti) and can be improved by all different thin films, starting with the 100 nm Ti coating and followed by the 100 nm TiN\textsubscript{x} coatings. In the case of the substoichiometric TiN\textsubscript{x} films the clear dependence on the nitrogen content in the film is evident. By the reduction of the nitrogen content in the film, the time for reaching the final contact angle decreases, which means faster wetting.

In literature a similar wetting behaviour for substoichiometric TiC films is predicted [2]. The wetting experiments with sputter deposited substoichiometric TiC films have started and the results of them will be published later.

2.2. Liquid Surface Energy Measurement

The estimation of the liquid surface energy \(\sigma_{LV}\) of molten metal drops can be done by measuring the drop geometry of a drop flattened due to gravity. In literature two empirical models are proposed for this determination (Dorsey et al and Koshavnik et al [6-8]). Both of them measure geometrical parameters of the drop (see figure 2), from which the liquid surface energy can be calculated. This measurement is only valid for non-wetting situations in immiscible systems, where the contact angel \(\theta\) is higher than 90° and for drops larger then a few millimetres in diameter.
Table 1. Contact angle and liquid surface energy of different metals.

|       | $\theta^a$ [°] | $\theta^b$ [°] | $\sigma_{LV}^b$ [mJ/m$^2$] | $\sigma_{LV}^c$ [mJ/m$^2$] | $\sigma_{LV}^d$ [mJ/m$^2$] |
|-------|----------------|----------------|----------------|----------------|----------------|
| Cu    | 144            | 145            | 1355           | 1028           | 1342           |
| Pb    | 128            | 142            | 462            | 541            | 413            |
| In    | 153            | 145            | 555            | 646            | 523            |
| Al    | 147            | 160            | 867            | 693            | 654            |

$^a$ measured values in the HTSDD
$^b$ literature values [2]
$^c$ Dorsey et al [6]
$^d$ Koshavnik et al [7]

The experiments were done on an inert GC substrate, which did not react with the liquid metals (except Al, but not in the short time of the measurement). The results of the contact angle and liquid surface energy measurements are summarized in table 1 which gives the comparison of our HTSDD results with the literature values. For Cu and In the experimental results are close to those given in literature. Pb and Al show stronger deviations which may be attributed to oxidation effects, impurity of the metals or other systematic errors. In addition it was found that the surface energy model according to Koshavnik provides more accurate results.

2.3. Reactive Wetting

Reactive wetting is the formation of a 3D reaction layer at the interface between the liquid and the solid. This formation can either lead to an interlayer which is more wettable than the substrate or to an interlayer which is less wettable than the substrate.

The interesting case for wetting promotion is the formation of a more wettable reaction layer. The spreading kinetics of reactive wetting has two limiting cases [2,9,10], depending on the time for the reaction at the triple line and the diffusion of reactant from the bulk drop to the triple line: Reaction limited reactive wetting (see figure 3a) and diffusion limited reactive wetting (see figure 3b).

In the first case diffusion is comparatively fast so the triple line chemistry is rate limiting resulting in a constant triple line velocity. In the second case the local reaction rates are comparatively high and
the reaction is limited through the diffusive supply of reactants from the bulk drop to the triple line. The decreasing contact angle during the experiment leads to a decreasing diffusion field, so a time dependent triple line velocity is expected.

The wetting behaviour of the CuABA® brazing alloy on three different materials was investigated: pure glassy carbon, GC coated with 100 nm Ti and GC coated with 100 nm TiN. The coatings were produced by sputter deposition; the sputter parameters are equal to those given in section 2.1.

The plot of the droplet radius vs. time is shown in figure 4. In all three different cases the approximation of the data points is a straight line, meaning constant triple line velocity and therefore identifying the reactive wetting type as reaction limited. The final contact angle of these three coatings is approx. 10° but as visible in figure 4 it takes different times to reach this final angle. (see also section 2.1, figure 1). The wetting on pure GC takes about twice the time than the wetting on the GC coated with Ti and TiN.

For substoichiometric TiNₓ films the spreading is too fast for a clear identification of the reactive wetting type in a droplet radius vs. time plot and therefore not shown.

Conclusions
In this paper three applications of a custom-built High Temperature Sessile Drop Device have been shown: the identification of the reactive wetting type, measurement of the liquid surface energy of metals and the contact angle study of substoichiometric films.

A wettability study of CuABA® on different substoichiometric TiNₓ films was done to gain information about the influence of nitrogen on wetting promoting TiNₓ coatings. A clear dependence of the wetting behaviour on the nitrogen content was found in our samples.

The liquid surface energy σLV was calculated for different metals according to two empirical models found in literature. Both of them calculate the surface energy from geometrical drop parameters in non-wetting and immiscible systems. One model was found to be more accurate.

The reactive wetting of the active brazing alloy CuABA® on GC, Ti and TiN was identified as reaction limited reactive wetting, which was concluded from a constant triple line velocity during the wetting experiment.

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