On the theoretical estimation of the contact angle in the PbO/Pb-system

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Abstract

In this paper we describe a new model to calculate the contact angle between liquid metals and ceramics. The results of this model are compared to theories established by other authors especially for the Pb/Pb(II)O-system.

To confirm the new model, experiments were made to determine the contact angle between lead and lead monoxide. By using the sessile drop technique we found that lead doesn't wet its monoxide Pb(II)O. The contact angle was measured to be $\theta_{\mathrm{Pb/PbO}} = 132^\circ \pm 2^\circ$, independent of applied ambient atmosphere and pressure.

Key words: interface wetting, metal foam

1 Introduction

The adhesion properties of solid particles have dominant influence on their practical use in metallurgy. One field where these properties play a role is the production of metallic foams via melt routes: a gas is introduced or in situ produced inside a liquid metal, for example aluminum. This causes the formation of bubbles and finally the build-up of a liquid metallic foam which in turn is solidified to give a solid porous metal. This metal foam represents a modern material and finds applications especially where low density combined with high stiffness or crash worthiness is required. For further details about production methods and applications, see [2–4,7].

Since stabilization mechanisms like disjoining pressure as in aqueous foams [8,9] are not applicable to metallic foams, the exact reason for their stability

is still unknown. It was found empirically, however, that the presence of small solid particles has a major influence : dependent on their size and adhesion properties they can enhance or diminish the stability of a liquid metallic foam [4].
Our research on the lead foam system [5] supports a stabilization model developed by one of the authors, [6]. In this model the formation of a particle layer on the surface of the bubbles in a liquid metallic foam is assumed. Due to the adhesion properties of these particles, a force towards the center of the bubbles is generated, acting in turn as a kind of disjoining pressure like in aqueous foams, keeping the bubbles from coalescing and thus stabilizing the foam.
While in melt route production processes these particles have to be added to the melt, this is not necessary in the powder metallurgical process used by us (described in [2]). Here small oxide particles originating from the starting powder serve as stabilizers. In the case of lead foams, during the foaming process, i. e. at temperatures of higher than 300°C, lead monoxide PbO can be assumed to make up the major amount of oxides, since the originally dominant $PbO_{1.44}$ [10] will convert entirely to PbO [11].
For the validation of the model adhesion properties of lead on lead(II)oxide are of importance. Since no data was available on this special system and theoretical predictions are contradictory, a measurement of the contact angle of the Pb-PbO system became inevitable.

2 Theoretical model to calculate the contact angle in the PbO/Pb system

2.1 Overview

Theoretical models usually describe the adhesion energy W between oxide ceramics and liquid metals, which is defined as:

$$W \equiv \sigma \cdot (1 + \cos\theta), \tag{1}$$

where σ is the surface tension of the liquid and θ is the contact angle. If the adhesion energy is known, the contact angle can be calculated, using the literature value of the surface tension of the liquid metal. For pure lead, which we used in our experiments, $\sigma = 458 - 0.13(T - T_m)\,[\mathrm{mJ/m}]^2$ according to [12].
The first semi-quantitative model of the adhesion energy in oxide/liquid metal systems was developed by McDonalds and Ebenhart [13] for alumina/liquid metallic systems. It divided the adhesion energy into the London-dispersion term, and the chemical term, being proportional to the Gibbs energy of forma-

tion of the oxide of the liquid metal. However, as this model was semi-empirical and applicable only for alumina, it can not be used to predict the adhesion energy in the PbO/Pb system.
Naidich [14,15] applied a very similar approach, but extrapolated it to all metal/oxide systems, by replacing the Gibbs energy of formation of the oxide by the difference in Gibbs energies of formation of oxides of the liquid metal and of the metal, treated as a cation of the oxide ceramic. In this way a semi-empirical graph is obtained [14,15], from which at $\Delta G = 0$ (which is the case for the Pb/PbO system) the contact angle should be around 60^o. This value can be considered as a first estimate for the requested contact angle, according to Naidich.
In 1985, Stoneham and Tasker proposed an image interaction model [16]. This quantum-mechanical approach has a good physical basis, and its development is very promising, but to our knowledge it has not been applied to the PbO/Pb system, and its application is not a straightforward task at all (for a recent review, see [17]).
In 1986, Chatain et al. [18] improved the McDonalds-Ebenhart model for alumina/liquid metal systems. The London dispersion interaction was neglected, but instead the metal-metal and the metal-oxygen interaction was considered even in non-reactive systems. Later, Wu et al [19,20] made a theoretical analysis, and derived theoretically the parameters, being similar to the semi-empirical parameters of [18]. Recently, Eustathopoulos and Drevet argued [21] that such a chemical model cannot be valid for a non-reactive system, and made a favorable conclusion for the image interaction model [16,17].
Eustothopoulos et al. [21,22] also divided all ionocovalent ceramic / liquid metal systems into reactive and non-reactive systems, based on the calculated solubility of oxygen in the given system. Based on experimental results obtained for alumina, they suggest the average contact angle of 127^o for all non-reactive ionocovalent ceramic / liquid metal systems. This value can be considered as our second possible estimate.

2.2 New model

In 2001, Kaptay and Báder [23] published a model for the adhesion energy of non-reactive liquid metal/oxide ceramic systems, based on the ion induced dipole – ion interaction model, which is physically very close to the image interaction energy concept [16,17]. This model was recently developed further by one of the authors [24]. The resulting equations are as follows:

$$W_{\mathrm{MO/Me}} = k_{\varepsilon}^2 \cdot \frac{2}{3} \cdot \frac{\alpha_{\mathrm{Me,g}}}{6} \cdot \frac{N_{\mathrm{Av}}}{\omega_{\mathrm{Me}}} \cdot \frac{z^2 \cdot e^2}{4\pi\varepsilon_0 \cdot (R_{O^{2-}} + R_{\mathrm{Me}})^4} \cdot \qquad (2)$$

Author	**Predicted Contact Angle**
Naidich [14,15]	60
Eustathopoulos et al [21,22]	127
Kaptay [24]	120

Table 1
Collection of predicted contact angle values in the PbO/Pb system, according to different theories

$$\cdot \left[1 + \frac{4}{6} \cdot \frac{\alpha_{\mathrm{Me,g}} \cdot \alpha_{\mathrm{MO}}}{(R_{O^{2-}} + R_{\mathrm{Me}})^6}\right]$$

where $\alpha_{Me,g}$ is the polarizability of the gaseous Me atom (for Pb: 6.8 10^{-30} m^3 [25]),
N_{Av} = 6.02 10^{23}1/mol, the Avogadro number,
z – the charge of the oxygen ion (z = 2),
e – the charge of the electron (= 1.60 10^{-19} C),
ε_o – the permittivity of the vacuum (=8.86 10^{-12} C^2/Jm),
$R_{O^{2-}}$ – ionic radius of the oxide ion (= 0.136 nm),
R_{Me} – atomic radius of the metal atom (for Pb: 0.175 nm),
ω_{Me} – molar surface area of the liquid metal (for Pb: 63,980 m^2/mol [26]),
α_{MO} – the polarizability of the ceramic, to be estimated from the Clausius-Mossotti equation as [27]:

$$\alpha_{MO} = \frac{3 \cdot V_{MO}}{4 \cdot \pi \cdot N_{Av}} \cdot \frac{n_{MO}^2 - 1}{n_{MO}^2 + 2} \tag{3}$$

where V_{MO} is the molar volume of the ceramic (for PbO: 23.4 cm^3/mol [28]), n_{MO} is the refractive index of the ceramic (for PbO: 2.6 [28], and from eq. 3: $\alpha_{\mathrm{PbO}} = 6.1 \cdot 10^{-30}$ m^3), k_ε is a semi-empirical parameter, characterizing the ceramic, being approximately equal for oxide ceramics. It is given by

$$k_{\varepsilon,MO} \cong 0,64 - 0,0739 \cdot \frac{I_{M^+}}{I_{O^{2-}}} + 0,0046 \cdot \left(\frac{I_{M^+}}{I_{O^{2-}}}\right)^2, \tag{4}$$

where I_{M^+} and $I_{O^{2-}}$ are ionic strengths of M^+ and O^{2-} ions of the ceramic, defined as the ratio of their charge to their ionic radius. For PbO, $I_{Pb^{2+}}/I_{O^{2-}}$ = 1.08, and so, from eq. (4): $k_{\varepsilon,PbO} = 0.566$. Substituting all the above constants into eq. (2), one finally obtains $W_{PbO/Pb} = 0.231$ J/m^2 = 231 mJ/m^2. Substituting into eq. (1) gives the predicted contact angle as $\theta = 120^o$. All values predicted by the different models are collected in table 2.2. One can see that the predictions made according to [21,22] and [24] are quite close. They are also close to the measured value, as will be shown below.

3 Description of the measurement equipment

The sessile drop method was applied to determine the contact angle between the PbO substrates and different Pb containing alloys. For the measurements of the contact angle a high-temperature vacuum furnace equipped with a Leitz optical system was used. The set-up consists of a horizontal cylindrical furnace (working up to 1200 °C) situated in a vacuum chamber connected to vacuum pumps and Ar or CO_2 gas. Before starting the experiments, at room temperature the chamber was evacuated down to $5{\cdot}10^{-8}$ bar, then filled with 1 bar of 99.999 % Ar or CO_2, respectively, then evacuated again to $5{\cdot}10^{-8}$ bar. In this way the residual partial pressure of contaminants around the sample was below 10^{-14} bar. During most of the experiments a CO_2 or Ar atmosphere was applied. In that cases after the first evacuation the system was refilled with the used gas.
After ensuring a clean atmosphere, the sample was melted, then gradually heated to the desired temperature with a heating rate of about 10 °C/minute. A first photograph was taken at room temperature of the solid piece of metal and the solid substrate. In the course of the experiment further photographs were taken corresponding to higher temperatures and changing of the shape of the sample. The photographs were taken by a CCD camera and the contact angle was measured directly from the enlarged images using a computer software with an accuracy better than ± 3°.
To measure the contact angle of the Pb/PbO-system, lead powder grains were melted on top of a PbO (yellow) substrate. The substrate was obtained from Pb(II)O-powder with a purity of better than 99.9% supplied by Merck. This powder was compacted at 20bar, which yielded discs with a diameter of 13mm and a thickness of 2–3mm.

4 Results

At first, two materials that were formerly used as precursor material for lead foams, were analyzed. This was done with the original powder grains with radius $r_g = 0.09$mm (called N-type in the following) and $r_g = 0.5$mm (L-type) as well as with hot pressed samples obtained from these powders. These materials show very different foaming behavior, which we attribute to the difference in particle size and oxide content, [29,30]. The oxide content was 2.4 wt.% PbO for the N-type material and 0.8 wt.% for the larger grains of the L-type precursor. In addition to these materials we also analyzed leadshot pellets supplied by Alfa Aesar (hence called Lα-type) with particle size $r_g = 1$mm and a metallic purity of at least 98% (as stated by the supplier). The oxide-content in this case was not known.

The measurements with the N- and the L-type material were not successful under any applicable conditions. We observed that the samples didn't take a spherical shape when melting, so that a measurement of θ was not possible. This behavior is most likely due to the remnant oxide skin on the surface of the samples.

In contrast, the Lα-material showed a reproducible behavior, see figure 1. The

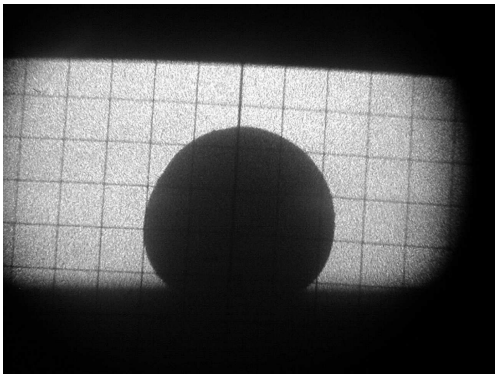

Fig. 1. *Photograph of lead shot pellet on PbO-substrate (see text).*

contact angle was determined from a number of 3 samples to be

$$\theta_{\mathrm{Pb/PbO}} = 132 \pm 2^{\circ} \tag{5}$$

The same results were obtained in air as well as under cleaned CO_2- and Ar-atmospheres. It was also observed that θ didn't vary significantly with time or temperature. A measurement under vacuum conditions $p < 10^{-5}$ mbar also produced no difference in θ.

5 Conclusion

The contact angle of the Pb/PbO-system was measured with the sessile drop method. The measurements were carried out in inert Ar and CO_2 atmospheres under normal and reduced pressure. We observed that a number of materials supplied by different companies couldn't be analyzed because of the oxide skin which could not be removed. However, data could be taken with leadshot pellets of 2mm in diameter and a metal purity of at least 98%. The contact angle was found to be $\theta_{\mathrm{Pb/PbO}} = 132^{\circ} \pm 2^{\circ}$, independent of ambient and pressure. This is rather close to the values predicted by the theoretical works of Eustathopoulos et al. [21,22] and Kaptay [24], while it differs by a factor of two from the works of Naidich [14,15].

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