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Contact Angle Measurement of Molten Lead-Lithium on Silicon Carbide Surfaces

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Measurements of the contact angles at the different temperatures of a molten lead-lithium eutectic alloy (PbLi) droplet on a silicon carbide (SiC) wall are needed for the research and development both of a magnetic confinement fusion (MCF) and an inertia confinement fusion (ICF) blankets. PbLi coolant/breeder flows in the coolant channel, which is made of the SiC walls, and will experience a flow slip at the wall, called as a magnetohydrodynamic (MHD) slip flow. The ICF blanket adopts a molten PbLi film flow along the first wall made of SiC. The PbLi contact angle database is necessary as the thermal property for numerically predicting the behavior of the flowing molten PbLi film. This study attempts the measurement of the contact angles between the molten PbLi and the various SiC surfaces. For examples, in order to examine the initial PbLi wettability, we measured the contact angles of a chemical vapor deposition (CVD) SiC, a nano-infiltration and transient eutectic-phase (NITE) SiC/SiC composites, and a NITE SiC in an inert atmosphere. We obtained the contact angle database of the molten PbLi, varying the temperature of PbLi from 250 to 400 ^{o}C, on a surface-polished as well as an unpolished SiC.

Keywords: Lead-lithium, Silicon carbide, Contact angle

1. Introduction

A contact angle database of a molten lead-lithium eutectic alloy (PbLi) droplet on a silicon carbide (SiC) is necessary for the research and development both of a magnetic confinement fusion (MCF) and an inertia confinement fusion (ICF) blankets.

In general, when a flow has a very thin momentum boundary layer on a hydrophobic or super-hydrophobic wall, the flow experiences a “flow slip” on the wall. In the MCF blanket, such as a dual-coolant or self-cooling liquid metal blanket, a liquid metal flow under a strong plasma-confining magnetic field is affected by the magnetohydrodynamic (MHD) force. Thus very thin momentum boundary layers form on the walls of the flow channel and perpendicular to the strong magnetic field (so called Hartmann layer). Its thickness δ_{Ha} in this strong magnetic field scales as $1/Ha$. Here, the Hartmann number squared Ha^2 expresses the ratio between the electromagnetic and the viscous force in the field. The theoretical and numerical study has suggested that the liquid metal flows bounded by the hydrophobic walls under the strong magnetic field may experience the flow slip at the wall, called as a MHD slip flow [1]. Eventually, it will affect the MHD flow instabilities, the MHD pressure drop and the heat and mass transfers in the fusion reactor blanket. The PbLi flows in the channels made of SiC, in a dual coolant lead-lithium (DCLL) blanket, are the typical example of the above case.

There are several experimental studies regarding the wettability of the molten PbLi with respect to a SiC plate, which have qualitatively demonstrated the poor wettability over a long period of time [2]. However, there has not been any quantitative research on the PbLi wettability until now. This study attempts to measure the contact angles formed between the molten PbLi to the various SiC walls, in order to develop a molten PbLi contact angle database. In addition to the contribution to the MCF blanket research, it is also helpful for the ICF blanket research, since the ICF blanket also adopts the PbLi film flow along the SiC first wall [3,4]. The PbLi contact angle database is necessary for the numerical studies of the behavior of molten PbLi film flow.

2. Contact angle measurement

2.1 Test materials

In this study, we employed the following materials: Chemical vapor deposition (CVD) SiC (from Rohm & Haas), Nano-infiltration and transient eutectic-phase (NITE) SiC/SiC composites [5,6], NITE SiC, and Titanium (Ti) plates. It is anticipated that a dense CVD SiC seal coat will be applied on any SiC composite components in a fusion reactor blanket [7, 8]. The NITE SiC/SiC composite was fabricated with reinforcement, using Tyrano^{TM}-SA SiC fiber cloth. The Tyrano-SA SiC is woven at 90^{o} two-dimensional crossings and is made by Ube Industrial Ltd., Japan. Ti is chosen as a reference material, since it is used as the wetting tip of the high-temperature ultrasonic Doppler velocimetry (HT-UDV) probe for the molten PbLi flows. HT-UDV probes require that the PbLi wets to the wetting tip, and the reference [9] reports that PbLi wets well to Ti.

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The contact angles can be affected by the droplet size as well as the surface conditions, including the surface roughness. The unpolished and polished surfaces of the test materials were prepared for the experiments. Their surfaces were observed by an optical microscope in order to examine the surface structure, and their surface roughness was measured by an atomic force microscope (AFM). The surface roughness measured by AFM was shown in Table. 1.

Table 1: Surface roughness measurements

	Unpolished [nm]	Polished [nm]
CVD SiC	**122**	**12.5**
NITE SiC/SiC	**72.5 (Matrix)**	**21.3 (Matrix)**
	660 (Fiber)	**127 (Fiber)**
NITE SiC	**N/A**	**21.5**
Ti	**346**	**47.8**

2.2 Chemical composition of PbLi

The PbLi eutectic alloy was fabricated by the Atlantic Metals & Alloys, Inc. The chemical composition of this PbLi alloy was examined by inductively coupled plasma–mass spectrometry (ICP-MS), and is shown in Table 2. The chemical composite was almost at the Pb-Li eutectic point (84.3 at% Pb & 15.7 at %Li, revised by Okamoto [10]). The percentage of impurities in the alloy was less than the detection limit of inductively coupled plasma–Auger electron spectrometry (ICP-AES).

Table 2: Chemical composition of PbLi

	Pb [at%]	Li [at%]
Before the test	**84.2**	**15.8**
After the test	**84.2**	**15.8**

2.3 Droplet preparation and image acquisition

Preparation and formation of the molten PbLi droplets were performed in an argon-filled glovebox, where the oxygen and the moisture were controlled to keep under less than 1 ppm. The PbLi ingot was melted in a melt pot, inside the glovebox, and then the oxides floating on the liquid surface were removed by using a metallic mesh. Molten PbLi droplets were formed on a stainless steel plate at room temperature, by using a pipette, so the globules immediately became solidified. After this, the contact angles of the PbLi droplets were measured with variation in diameter of the droplets, from around 2 mm up to 5 mm. The preliminary testing showed that the contact angles of the PbLi droplets got saturated with respect to the droplet diameter, over the values of around 3 mm. We chose the droplet diameters of over around 3 mm, as the appropriate size for the PbLi contact angle measurement. The solidified PbLi droplet in the appropriate size was put on the test material and heated from below with an electric heater, so that the solidified PbLi droplet melted and became the molten PbLi droplet, on top of the test material. After confirming that the PbLi melted, the images of the PbLi droplets were taken by a digital camera installed outside of the glovebox. The bulk temperature of the PbLi droplet was measured by inserting a thermocouple into the PbLi droplet after taking the image.

2.4 Image analysis

The digital images of the PbLi droplets were analyzed to get the contact angles by using the interface analysis software FAMAS (interFAce Measurement & Analysis System by Kyowa Interface Science Co., Ltd.). In this study, we employed the tangential line method to determine the contact angle; since the trace line of the droplet surface from the contact line where the three phases (gas, liquid and solid) meet was too steep, the θ/2 method could not be applied to the PbLi images. The tangential trace line of the PbLi droplet was determined based on the circles calculated from 3 surface-tracing markers on the droplet surface. The tangential line was then used to determine the contact angle (e.g. Fig.1). The errors in the contact angle measurements mainly resulted from the inaccuracies in the contact line location. The horizontal error bars in the measurement results were made based on ±1 pixel horizontal displacements from the most probable position. The vertical error bars in the measurement results were due to the initial measurement errors in the thermocouples.

2.5 PbLi droplet oxidation

Even though the PbLi droplets were formed in the inert glovebox, some very small solid particles still gathered on the droplet surface to form a solid shell about 5 minutes later. The solid particles significantly affected the contact angle measurement. Therefore, after taking an image of the droplet, each PbLi droplet was replaced, in order to mitigate the impurities effects on the contact angle as much as possible. Plus, in order to identify the chemical compositions of the solid particle, an X-ray diffraction (XRD) analysis was carried out. The results of the analysis are shown in the following section.

The PbLi corrosion can affect the contact angles by enhancing the wettability of the molten PbLi. The contact angle is measured after long-term wetting to predict the PbLi wetting behavior in a fusion blanket operation. However, the change of the PbLi contact angle could not be monitored over time because of the PbLi surface oxidation.

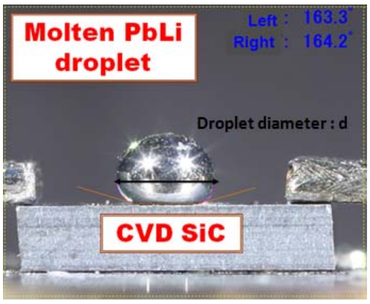

Fig.1 a molten PbLi droplet on a CVD SiC (the droplet diameter: 3.2 mm)

3. Results

3.1 Investigation of the PbLi oxides

An X-ray diffraction (XRD) technique was employed to identify the chemical composition of the solid particle. The specimen was prepared in the inert glovebox by maintaining the molten PbLi at 300 °C for around 16 hours before cooling it down, forming a solid particle layer on the molten PbLi. After this treatment, the specimen was packed in the glovebox and transferred to the inert XRD analyzer. We do this in order to avoid the surface oxidation, which happens even at room temperature. The surface of the specimen partially turned to black after cooling. On the observation, Pb, LiOH-H_2O and slight amounts of PbO were detected on the black surface. The rest of the specimen was composed of Pb, PbO and slight amounts of Li_2PbO_3.

We hypothesize that the LiOH was formed on the specimen surface through the following chemical reaction:

$$Li_2O + H_2O \rightarrow 2LiOH \qquad (1)$$

Therefore, Li_2O is expected to exist in the PbLi specimen from the beginning of the experiment. Li_2O is also expected to be found in the molten PbLi due to the oxidation in the glovebox. Due to the difference of specific densities (buoyancy effect), Li_2O accumulates on the surface of the molten PbLi. According to our hypothesis, it is expected that Li_2O reacts with H_2O and solidifies. After solidification, LiOH absorbs another H_2O to be LiOH-H_2O, and then the temperature drops below 100-110 °C. Based on this analysis, the solid particles on the molten PbLi droplet consist of mainly LiO_2 or/and LiOH.

Our analysis shows that the bulk molten PbLi contains some amount of PbO, despite the presence of many Li atoms in the molten PbLi. The specific density of PbO at room temperature is around 9.53, which is close to the 9.49 of PbLi (at 300 °C). We infer that PbO exists uniformly in the bulk, and small quantities of PbO exist on the liquid surface, due to the difference in the specific density.

3.2 PbLi contact angle measurements

Figures 2 to 5 show the measurements of the contact angle of the molten PbLi with the various SiC as well as Ti. The molten PbLi does not wet any kind of SiC or Ti, in the temperature range of 250-400 °C, given an exposure time of around 20 seconds.

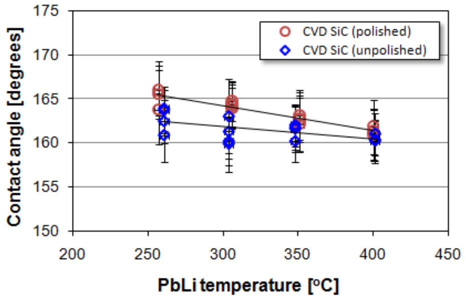

Fig.2 Contact angle for molten PbLi on CVD SiC

The contact angles are greater than 150°, and are hence classified as the super-hydrophobic. The difference in the surface roughness has no effect on the contact angle, given an exposure time of around 20 seconds. In addition, the microstructure of the NITE SiC/SiC composite showed a little change of the contact angle, as shown in Fig. 4.

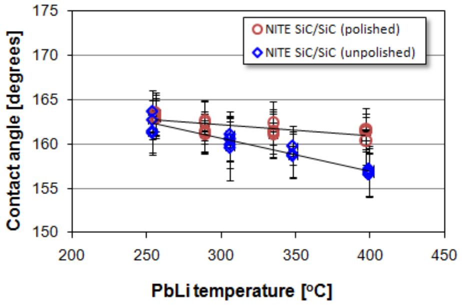

Fig.3 Contact angle for molten PbLi on NITE SiC/SiC composite

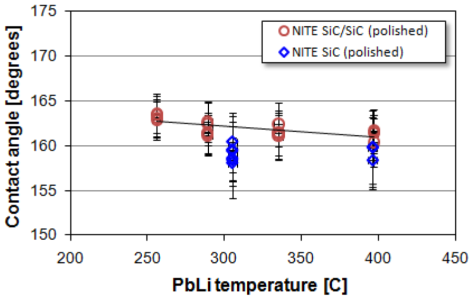

Fig.4 Contact angle for molten PbLi on NITE SiC (polished plate)

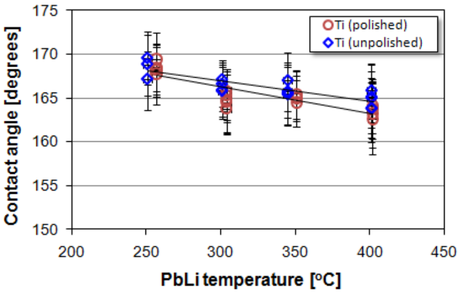

Fig.5 Contact angle for molten PbLi on Ti

4. Discussion

4.1 Relation of contact angle of PbLi to temperature

The contact angle of the molten PbLi is dependent on the temperature, and this was observed in the present study for both Ti and the various SiC. The relationship between the temperature and the contact angle can be expressed using the Young-Laplace equation as follows [11];

$$\left(P_l - P_g\right)\overrightarrow{e_n} = \frac{2\sigma}{R}\overrightarrow{e_n} + \left(\frac{\partial\sigma}{\partial T}\cdot\frac{dT}{ds}\right)\overrightarrow{e_s} , \qquad (2)$$

where P_l: internal pressure, P_g: external pressure, σ: surface tension of the liquid, R: droplet radius, T: liquid temperature, s: curvilinear coordinate along the droplet surface, e_n: normal unit vector, e_s: tangential unit vector, and contact angle: θ. The second term on the right hand side is the Marangoni term. We use the Young-Laplace equation instead of the Young equation, since the Young equation is based on a local thermodynamic equilibrium condition at the contact line between the liquid, solid, and gas phases.

The temperature dependency of the PbLi surface tension is $\partial\sigma/\partial T<0$ (the gradient is constant) [12]. We hypothesize that the temperature gradient: dT/ds may exist along the curvilinear direction: the droplet surface, and have a negative sign and eventually the absolute value of dT/ds may become larger, when the molten PbLi temperature is higher. Because of this, the Marangoni term: the sign of $(\partial\sigma/\partial T)\cdot(dT/ds)$ is positive, and is expected to be intense at higher temperatures of the molten PbLi. Since the droplet seems to be axially symmetric, a vertical-lift component of the Marangoni term remains. The lift force caused by the Marangoni term integrated over the droplet surface slightly elongates the droplet in height, as result the contact angle decreases. This is shown in Fig. 6. Through the evaluation of the Marangoni term, we infer that the droplet-lift effect is intense at higher temperature of the droplet, to relax the steep curvature of the droplet near the contact line, so that the contact angle decreases as the droplet temperature increases.

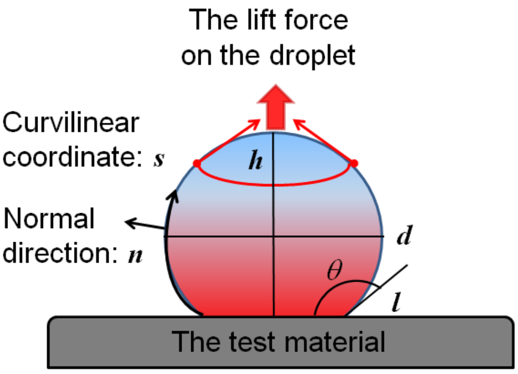

Fig.6 Relation of contact angle of PbLi to the temperature

We analyzed the shapes of the PbLi droplets, with respect to droplet diameter: *d*, droplet height: *h*, the diameter of the contact zone: *l*. According to the image analyses, we found that *h* slightly increased as *l* slightly decreased, when the molten PbLi temperature elevated. Here is a good example data; the ratio of the droplet height over the diameter of the contact zone (h/l) changed from about 1.08 to 1.16, as the droplet temperature increased from about 260 to 350 °C, in the case of the unpolished CVD SiC. The results of this analysis support our explanation of the contact angle dependency on the droplet temperature.

4.2 Effects of corrosion on contact angle

It has been reported that the molten PbLi wets to Ti [9]. The smaller contact angle is expected to form between the molten PbLi and Ti after the molten PbLi has had a longer exposure, due to serious corrosion of the molten PbLi. Plus, it has been reported that an adhesion layer was formed on the NITE SiC/SiC composite after the molten PbLi was wetted at 900°C for about 1000 hours [2]. Therefore, the initial contact angles of the molten PbLi on SiC surfaces, as well as Ti surface, are expected to differ after the longer exposure, due to the corrosion.

4.3 MHD slip flow of PbLi on the hydrophobic surface

If the MHD slip flow occurs, its slip length can be comparable to, or even larger than δ_{Ha}. The slip length is defined as an extrapolated distance relative to the wall, where the tangential velocity component vanishes. The thickness of the Hartmann layer in the liquid metal flow is about 1 μm for a 10 T magnetic field. This is typical of future fusion reactors, for example. The slip length can vary from nanometers to micrometers or even tens of micrometers, for specially designed super-hydrophobic surfaces [1]. The combination of the molten PbLi and various SiC is super-hydrophobic; therefore the slip length is expected to the same order of the magnitude as that of other hydrophobic or super-hydrophobic surfaces, and to be comparable to the thickness of the Hartmann layer under a strong magnetic field. Based on this, the MHD PbLi slip flow can occur on the super-hydrophobic SiC surfaces under strong magnetic fields.

5. Conclusion

The contact angles formed between the molten PbLi and the various SiC were determined experimentally.

1. All combinations of the molten PbLi and the various SiC and Ti are initially super-hydrophobic, in the temperature range of 250-400 °C. The difference in the surface roughness (as shown in Table 1) has little effect on the contact angle. However, it is expected that the contact angles differ with the surface roughness, if PbLi corrosion occurs.
2. Based on the XRD analysis, it is expected that the solid particles consist of mainly LiO_2 or/and LiOH, and that the bulk molten PbLi contains some amount of PbO, despite many Li atoms being contained in the molten PbLi.
3. This study also shows that the MHD PbLi slip flow can occur on the super-hydrophobic SiC surfaces under certain strong magnetic fields.

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