

Evaluation of unusual change in contact angle between MgO and molten magnesium

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Abstract

The wetting of MgO by molten magnesium was measured between 973 and 1273 K using an improved sessile drop method. In this method, molten magnesium was set around the sample droplet to prevent oxidation of the magnesium droplet. A significant volume loss of the droplet was observed over 1073 K due to the high vapor pressure, and the contact angle was underwent an unusual change over 1173 K. The contact angle first decreased and then increased. This phenomenon occurred due to the pinning of the three-phase line at deep ditch. This change in the contact angle is an apparent change in contact angle. The intrinsic contact angle should be decided using the initial value or the maximum value just before the disappearance of the droplet. For any high vapor pressure system, such a change in contact angle can be observed at high temperatures.

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1. Introduction

Magnesium has various useful characteristics as well as the lowest density of practical metals. Recently, it has become into use in various fields. In particular, magnesium based composites are expected to be useful for automobile parts. The wetting of ceramics by molten metal is one of the most important phenomena for various applications such as the production of composite materials. However, the wetting measurement by magnesium is very difficult. One of the reasons is the oxidation of magnesium. If an oxide film exists on the surface of the sample, the obtained contact angles will be incorrect. The other reason is the very high evaporation pressure of magnesium. Fig. 1 shows the evaporation pressure curve of magnesium [1]. Although the wetting of ceramics by molten metal have been reported by many researchers [2–11], only a limited number of studies [12–14] have been reported on the wetting by molten magnesium. Shi et al. investigated the wetting of carbon, AlN [12], alumina, iron, and stainless steel [13] by molten magnesium at 973 and 998 K. However, it was not measured at high temperatures. Contreras et

al. investigated the wetting of TiC by molten magnesium at 1073, 1098 and 1173 K [14]. In their study the magnesium droplet might be oxidized because an ordinary argon gas was used for the atmosphere.

In order to simplify the wetting phenomena, MgO was selected as the substrate in this study. Its wetting by molten magnesium was investigated at a low oxygen partial pressure in a wide temperature range between 973 and 1273 K. In order to prevent oxidation of the magnesium droplet, the droplet was covered by magnesium vapor generated from another source. In addition, an evaluation method for the wetting by a liquid with a high vapor pressure is also discussed.

2. Experimental procedure

The liquid metal sample used in this study were 99.98% pure magnesium (Nilaco Co., Japan). Other magnesium rods with the same purity was placed around the sample for evaporation to reduce the oxygen partial pressure. The substrate was 99% MgO (Nikkato Co., Japan). Three magnesium pieces weighing a total of about 0.3 g were cut from a 1.6 mm diameter rod. The MgO plate had dimensions of 20 mm × 20 mm × 5 mm. One side of the plate surface was polished to an average roughness of

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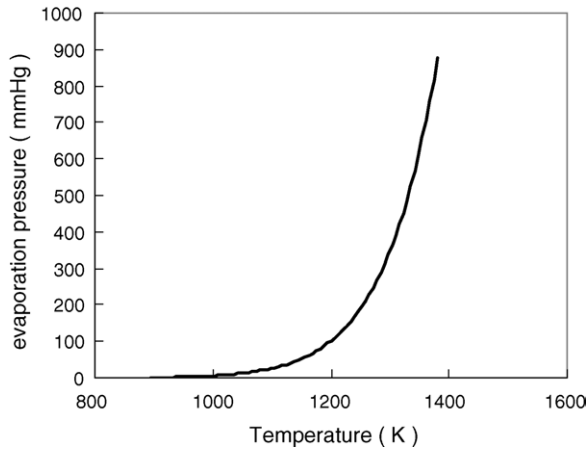


Fig. 1. Mg evaporation pressure curve.

100 nm, which was measured by a surface profilometer (Dektak 3, Japan). Both the MgO plate and the magnesium sample were carefully cleaned in acetone using an ultrasonic machine before placing in the apparatus.

An improved sessile drop method [3,4] was used in this study. Fig. 2 shows a schematic diagram of the experimental apparatus.

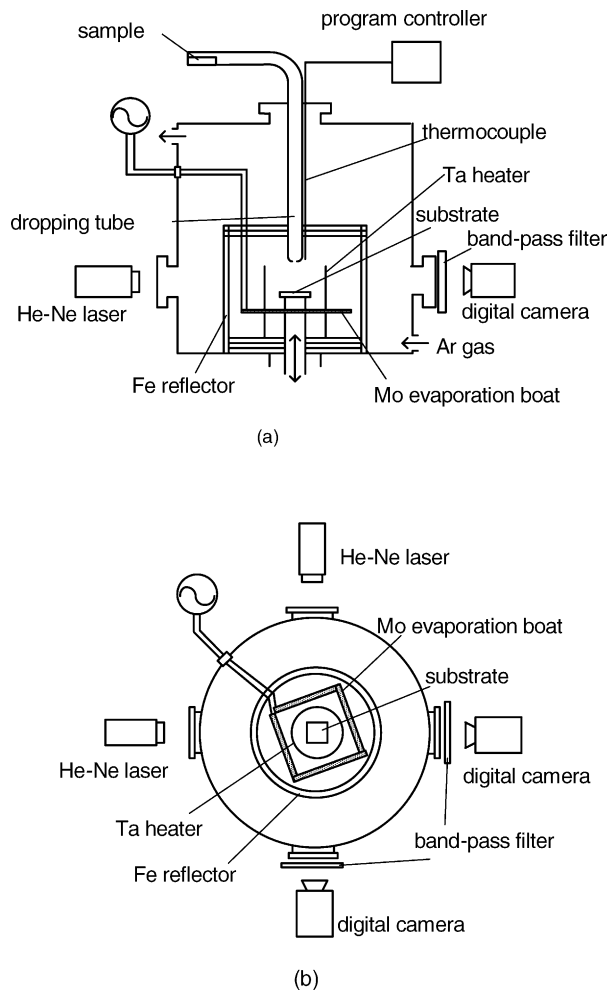


Fig. 2. Schematic of experimental apparatus.

The improved sessile drop apparatus system consists of a sealed chamber, tantalum heater, iron reflectors, an evacuating system with a rotary pump and a turbo molecular pump, a MgO dropping tube, a programmable temperature controller, K thermocouple (Ni–10% Cr/Ni–Mn), two He–Ne lasers, two band-pass filters and two high-resolution digital cameras with 2000×1312 pixels. The band-pass filter passes only laser beam (632 nm). Two digital cameras and two He–Ne lasers can ensure the droplet symmetry.

After the MgO plate was placed in a horizontal position under the dropping tube, a magnesium sample was put into the glass tube and magnesium rods for the evaporation [12,13] were placed in Mo evaporation boats around the Ta heater. Before the temperature is raised, the chamber was evacuated to about 4×10^{-4} Pa. Purified Ar gas flowed into the chamber during heating. The sample was heated to the measurement temperature in Ar atmosphere at the heating rate of $20^\circ\text{C}/\text{min}$. After the sample temperature reached the desired temperature, Ar gas was stopped flowing into the chamber. The sample magnesium was then inserted into the bottom of the MgO tube and kept there for 90 s to be melted. The molten magnesium was pushed out through the small hole (diameter = 1 mm) at the bottom of the MgO tube and dropped onto the MgO substrate. The initial oxide of the Mg surface can be removed when passing through the small hole. At the same time, a current of 30 A (surface temperature was about 1023 K) was flowed in the Mo evaporation boat in order to fill the chamber with magnesium vapor. As soon as the sample was dropped on the substrate, photos were also taken from two directions and defined as the drop profile at zero time. After the first photos, photos were taken at regular intervals for 1800 s. The photographs captured by a computer were analyzed using an axisymmetric-drop-shape-analysis program to calculate the contact angle, surface tension and density. Two or more experiments were performed at the same temperature to confirm the repeatability. The surface roughness and line roughness after the experiments were measured by a laser 3D profile microscope (Keyence, VK-8550, Japan) and a surface profilometer (Dektak 3, Japan). The chemical reactions at the interface were identified by X-ray diffraction (XRD).

3. Results and discussion

3.1. Effect of magnesium vapor

The effect of the magnesium vapor on the appearance of the magnesium droplet is shown in Fig. 3. These photographs were taken without the He–Ne laser at 973 K. When the magnesium vapor is generated, a metal luster was observed on the droplet surface throughout the experiment (for 1800 s). Thus, the oxidation of the droplet was prevented by the magnesium vapor. When magnesium vapor was not generated, the oxide film was formed on the droplet surface and the metal luster disappeared within 300 s after the dropping. If the measurement temperature was at 1073 K or over, no oxide film was observed even without the generated vapor due to the evaporation of the droplet itself.

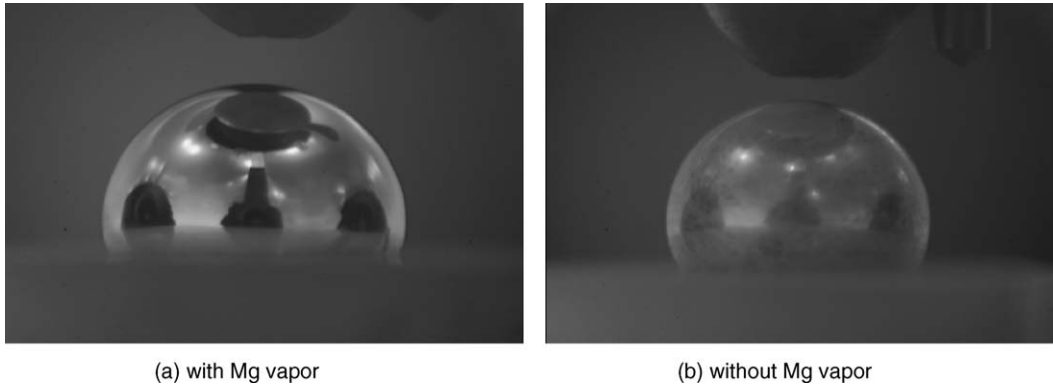


Fig. 3. Effect of Mg vapor on surface appearance of Mg droplet.

3.2. Change in contact angle with time

Fig. 4 shows the variations in the contact angle of the molten magnesium on MgO between 973 and 1273 K. At 1273 K, the measurement was performed until the droplet completely disappeared due to the droplet evaporation. Although the contact angle does not change at 973 K, it monotonically decreases at 1073 K. An unusual change in the contact angle was observed over 1173 K. The contact angle first decreases and then increases. Fig. 5 shows the relationship among the interfacial diameter, the droplet height and the contact angle. Because the Mg–MgO system is a non-reactive system, all of the contact angle, the interfacial diameter and the droplet height do not change. However, the contact angle at 1073 K decreases due to the droplet evaporation. At 1173 and 1273 K, there are three phases. In phase I, the contact angle keeps decreasing to a minimum value. In phase II, the contact angle keeps increasing to the maximum value. In phase III, the contact angle suddenly decreases because the droplet disappears. Fig. 6 shows a schematic model showing the contact angle change in each phase. Fig. 6(a) and (b) corresponds to phase I and phase II, respectively. In phase I, the interfacial diameter does not change while the droplet height decreases. As a result, the contact angle decreases, as shown in Fig. 6(a). In

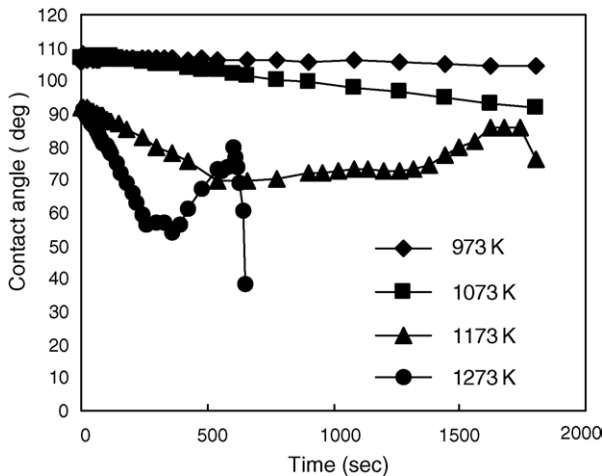


Fig. 4. Variation in contact angle of Mg/MgO with time between 973 and 1273 K.

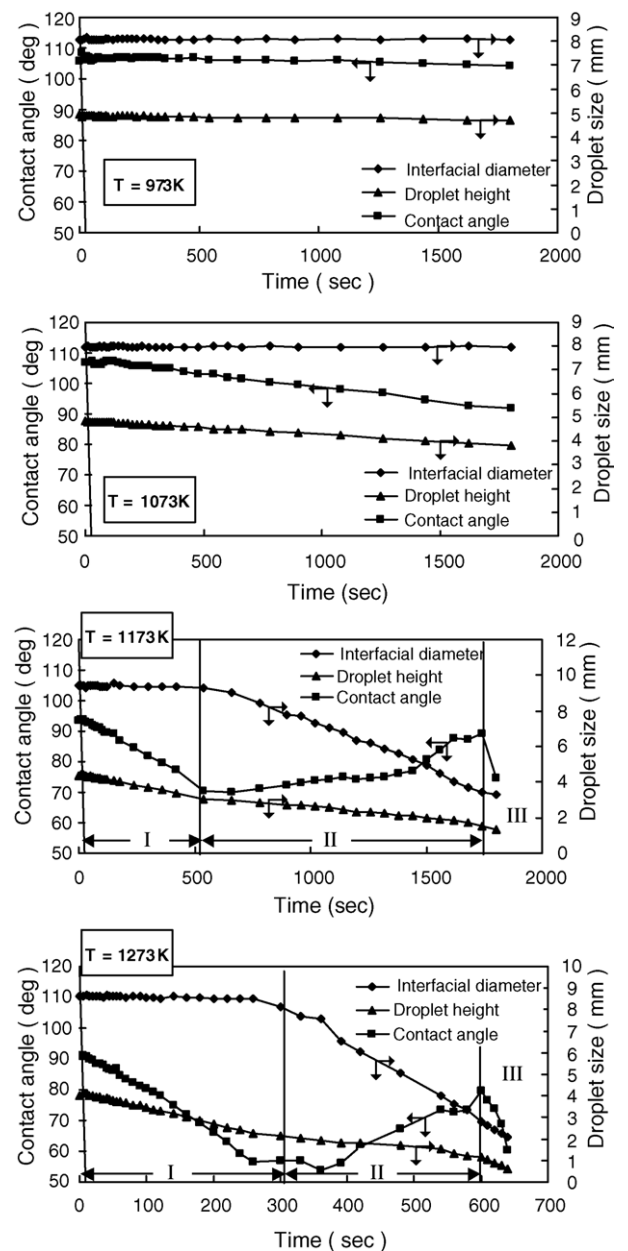


Fig. 5. Relationship of interfacial diameter, droplet height and contact angle of Mg/MgO between 973 and 1273 K.

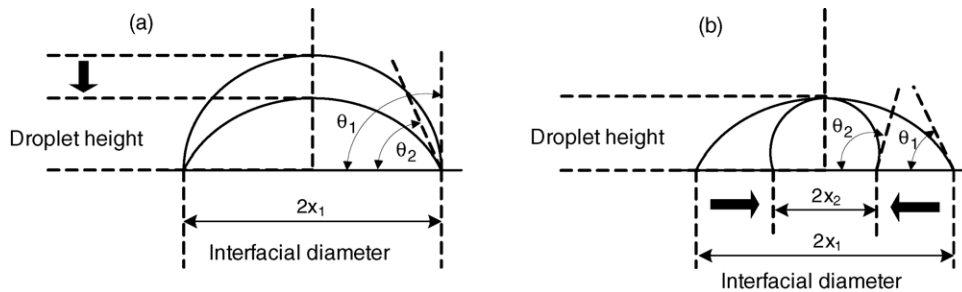


Fig. 6. Schematic illustration of the contact angle.

phase II, the interfacial diameter starts to decrease. On the other hand, the droplet height stops to change as shown in Fig. 6(b). The contact angle in phase II increases. In phase III, the droplet is disappearing. Both the interfacial diameter and the droplet height decrease. At 1073 K, only phase I occurred for 30 min.

The MgO substrate after the wetting experiment was analyzed by a laser 3D profile microscope and a surface profilometer in order to clarify the mechanism of this phenomenon. Fig. 7 shows the edge surface where the droplet initially existed. Table 1 shows the surface roughness of the squares ($30\ \mu\text{m} \times 30\ \mu\text{m}$) corresponding A–D in Fig. 7. The surface roughness increases near the three-phase line where the droplet initially existed. Fig. 8 shows its surface profile. Deep ditches were observed near the three-phase line. Therefore, the interfacial diameter did not change because the droplet was fixed at the deep ditch. However, when the contact angle decreases to a certain extent, the droplet moves inside to get over the deep ditch. As a result,

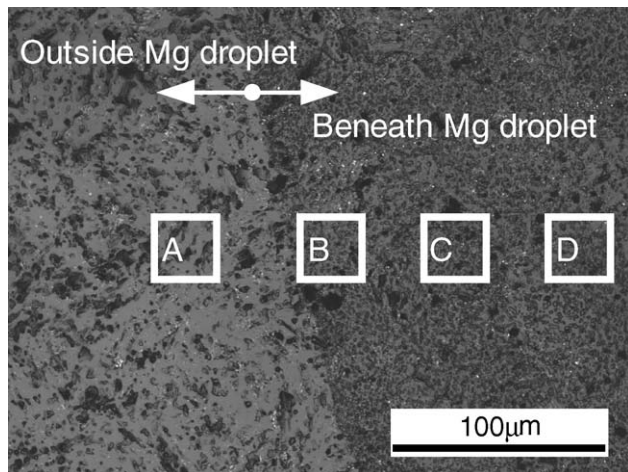


Fig. 7. Microstructure of edge surface after disappearance of droplet at 1273 K.

Table 1
Surface roughness (μm) variation on the surface shown in Fig. 6

A	0.102
B	0.194
C	0.595
D	0.267
Before experiment	0.098

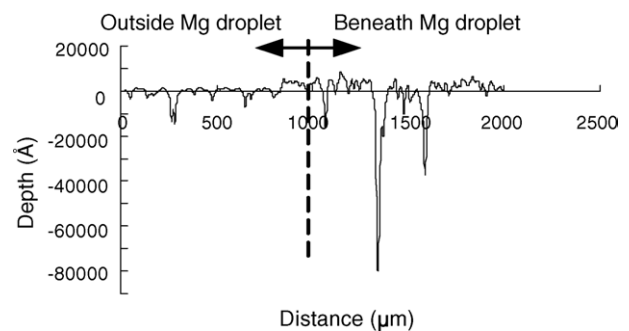


Fig. 8. Surface topography of edge surface after disappearance of droplet at 1273 K.

the contact angle starts to increase. After the complete evaporation of magnesium, no reaction phases were found on the substrate by XRD. Thus, the unusual change in contact angle at 1173 and 1273 K was not caused by interfacial reactions. In other words, the phenomenon was not intrinsic, but an apparent contact angle variation due to the volume loss of the droplet. For the high evaporation systems, the intrinsic contact angle in the Mg/MgO should be the initial contact angle value. As shown in Fig. 4, after the three-phase line gets over the deep ditch, the contact angle increases toward the intrinsic value. However, the contact angle does not often reach to the intrinsic value because the evaporation is so fast that the droplet disappears before the three-phase line reaches to the equilibrium location. In addition, the difference between the maximum value and the intrinsic value can be larger when the surface roughness of the substrate increases. In a reactive system, the maximum contact angle just before the disappearance should be the most important for estimating the intrinsic equilibrium contact angle after the reaction.

4. Conclusion

The wetting of MgO by molten magnesium was investigated between 973 and 1273 K using the sessile drop method. Molten magnesium was placed around the sample droplet in order to prevent oxidation of the droplet. Although the contact angle does not change at 973 K, the contact angle monotonically decreases at 1073 K. An unusual change in the contact angle was observed at 1173 and 1273 K. These changes were caused by the significant evaporation of the droplet. In this case, the droplet interfacial

diameter does not change while the contact angle is decreasing. When the droplet three-phase line moves inside to get over the deep ditch, the contact angle starts to increase. Namely, in this system, an apparent change in the contact angle is easily observed by volume loss of the droplet. The intrinsic contact angle should be constant and close to the initial value or the maximum value just before the disappearance of the droplet.

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