

Trial to Evaluate Wettability of Liquid Zn with Steel Sheets Containing Si and Mn

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Since it has been pointed out that liquid Zn alloy sometimes exhibits non-wetting behavior on high-tensile strength steels usually containing Si and Mn, there have been several studies to improve the wettability of liquid Zn. Although those studies evaluated the wettability qualitatively by observation of the surface of galvanized steels or exfoliation testing of Zn on steel substrates, it is further required to evaluate the wettability of liquid Zn on steels by measuring the contact angle, work of adhesion, spreading velocity *etc.* which are usually used to assess the general wetting behavior. In the present work, we applied a sessile drop method to measure the change in contact angle and diameter of liquid Zn droplets wetted on steels containing Si and Mn with time to evaluate quantitatively the dynamic wetting behavior of liquid Zn on steel substrates.

KEY WORDS: wetting; high tensile strength steel; sessile drop method.

1. Introduction

Galvanizing is one of the most useful procedures for preventing the corrosion of steel sheets. There has been a lot of fundamental research on the wettability of liquid Zn on the surfaces of steel sheets or films.^{1–8)} For example, it has been reported that the addition of Al to a liquid Zn bath leads to an improvement in the physico-chemical properties of Zn films, and that pre-Ni plating the steel substrate leads to good wettability of liquid Zn on steel sheets. For those galvanizing procedures, it has been known that several bad wetting behaviors occur for high-tensile strength steels containing Si and Mn, which have been developed for the automobile industry to improve fuel consumption and safety *etc.* It has been pointed out that one of the reasons for the bad-wettability associated with high-tensile strength steels is related to the formation of oxides of Si and Mn on the steel surface. In order to address this bad-wettability, it is indispensable to understand the wetting behavior of liquid Zn on steel sheets in detail. Thus, many investigations have been reported so far on the wettability of liquid Zn on steels containing Si and Mn.^{3–8)}

Generally, the wettability of liquids on solid surfaces is evaluated from an equilibrium contact angle measured by the sessile drop method. For a system, where no chemical reaction occurs, the contact angle is determined from the balance of the surface tensions of the liquid and solid surfaces with respect to the interfacial tension between the solid and liquid phases. When the contact angle is smaller

than 90°, this is called good-wettability. On the other hand, it is impossible to measure the equilibrium contact angle when the steel surface reacts with liquid Zn to form intermetallic compounds, because the liquid droplet spreads due to alloying reactions. For the wettability of liquid Zn on steels, there have been some qualitative evaluations such as counting the number of defects with bad-wetting after galvanizing. Although a few reports have been given to address the change in contact angle of the liquid Zn droplet on an iron substrate by the sessile drop method,^{9–11)} no methods have yet been established to quantitatively evaluate the dynamic wetting behavior of liquid Zn on steel substrates with different chemical compositions.

In the present paper, we have tried to quantitatively evaluate the dynamic wetting behavior of liquid Zn on steel substrates from observations of the change in droplet shape and contact angle of liquid Zn on the steel substrate using a high speed camera to take images just after contacting a droplet on the substrate. Then, we defined the following two quantitative properties: one of them is an initial contact angle which corresponds to the equilibrium contact angle of liquid Zn on a steel substrate before alloying reactions occur by measuring an average contact angle just after Zn droplet attaches with the substrate. The other is a spreading velocity of liquid Zn droplet on the steel substrate, which is determined from the change in the diameter of a droplet caused by spread-wetting as well as by alloying reactions. From these two quantitative properties, we have tried to evaluate the dynamic wetting behavior of liquid Zn on steel

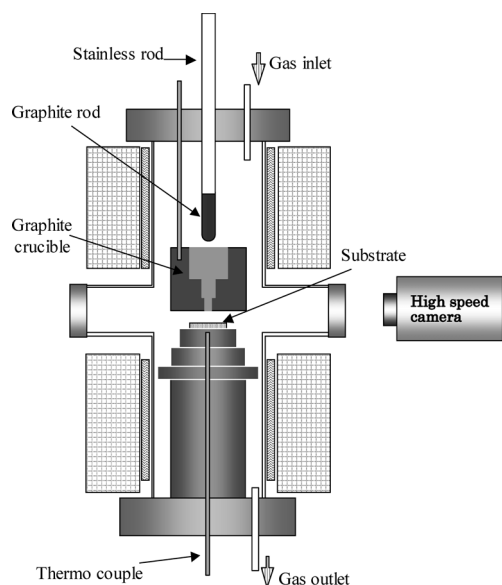


Fig. 1. Schematic diagram of experimental setup of sessile drop method.

sheets containing Si and Mn.

2. Experimental

In the present work, we carried out the wetting experiments for low-carbon steel (Fe-0.13mass%Mn) and steels containing Si and Mn (Fe-1.0mass%Si-1.0mass%Mn). These specimens were prepared in a vacuum melting furnace. After the specimens were hot-rolled (soaking temp.: 1230°C, finishing temp.: 900°C, coiling temp.: 720°C) and then cold-rolled (4 mm→1.0 mm), a specimen with 1 mm×20 mm×20 mm was prepared as a substrate. In order to remove the oxides from the surface of the specimen, the specimen was polished using emery paper #1500 and alumina powder, and finally dried once all the oil had been removed from the surface. A schematic diagram of the experimental apparatus for performing the wetting observations is shown in Fig. 1. Briefly, the specimen as a substrate is set on a graphite support stand in the center of the furnace, and a graphite crucible for melting Zn is set above the substrate. There is a hole with a diameter of 1.5 mm ϕ at the bottom of the crucible, through which liquid Zn droplets can be dropped from the crucible onto the substrate beneath. In order to prevent Zn vapor depositing on the observation windows of the furnace, the crucible was sealed with a lid. After setting the substrate and filling the crucible with the Zn specimen, the atmosphere in the furnace was then replaced by H₂ gas, and the specimen and substrate heated up to 600°C according to the profile in Fig. 2. After keeping the specimen for 30 min at 600°C, a Zn droplet was then dropped on the substrate. The temperature of the crucible and the substrate can be controlled separately from two independent heating elements made of Ni-Cr wires. The temperature (600°C) and the atmosphere (H₂ gas) were selected to prevent the formation of oxides on the surface of the substrate and on the liquid Zn after several pre-experiments had been conducted. Although those experimental conditions are different from the known industrial conditions, we have paid close attention to prevent the formation of oxide

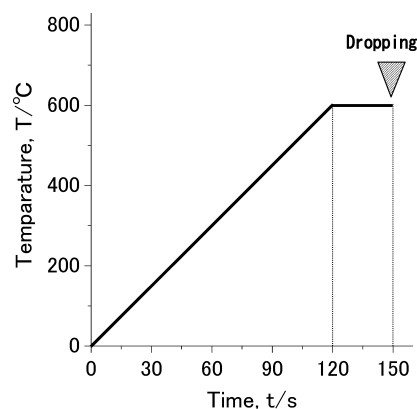


Fig. 2. Temperature profile of the experiment.

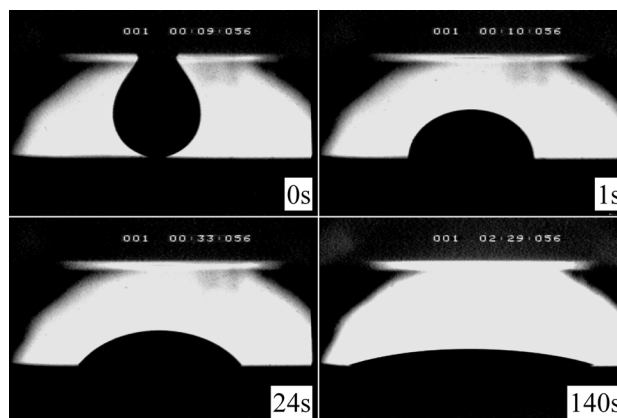


Fig. 3. Change in droplet shape of liquid Zn on steel sheet containing Si and Mn.

on the surface of the small Zn droplets to establish a method to quantitatively evaluate the wetting behavior of liquid Zn on steel sheets containing Si and Mn.

3. Experimental Results and Discussion

3.1. Evaluation of Contact Angle

Figure 3 represents one example of the spreading behavior of a Zn droplet on a steel sheet containing Si and Mn. The droplet was dropped from the crucible which was set 6 mm above the substrate. Figure 4 shows the change in contact angle of the droplet with time just after dropping the droplet. The change in the contact angle of the droplet is also shown in Fig. 5 from the time 0.1 s after dropping the droplet until the contact angle was less than 10°. Figures 4 and 5 correspond to the experimental results obtained for two kinds of specimens, that is to say, low-carbon steel and steel containing Si and Mn. In these figures, the plots indicate the experimental results obtained twice for the above two kinds of steels. As shown in Figs. 4 and 5, the contact angle decreases with time, and finally falls below 10°. Generally, when the contact angle is less than 10°, the diameter of the droplet increases to over 10 mm, which cannot be observed using the present experimental apparatus. Figures 4 and 5 show that the droplet vibrated for a while just after being dropped on the substrate, but gradually the vibration subsided and the droplet started to spread due to both spread-wetting and alloying reactions.

In Fig. 4, during the vibration of the droplet, of which the

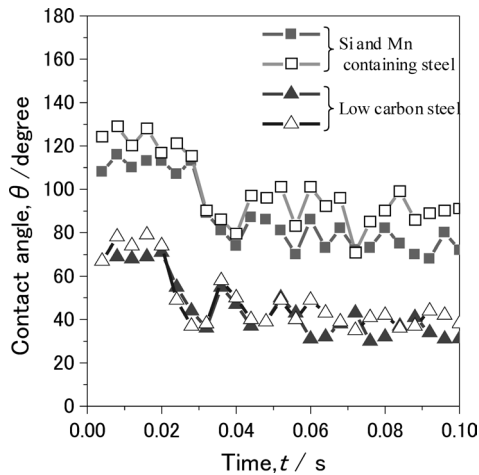


Fig. 4. Change in initial contact angle of liquid Zn on low-carbon steel and Si-Mn steel with time.

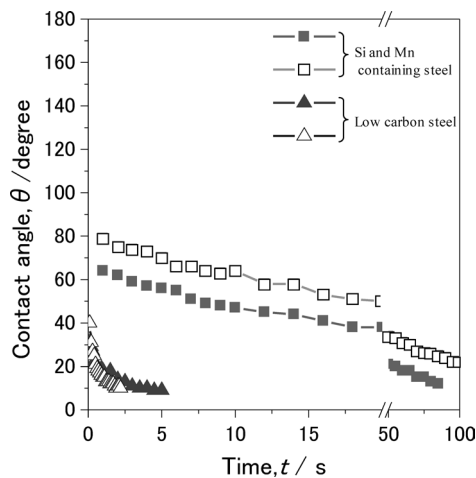


Fig. 5. Change in contact angle of liquid Zn on low-carbon steel and Si-Mn steel with time.

amplitude was almost constant, the contacting area between the droplet and the substrate increased and decreased repeatedly. This phenomenon indicates that there is no alloying reaction between the droplet and the substrate. When the alloying reaction starts to occur, the contacting area does not return from large value to the original small one, and then the contact angle gradually becomes smaller. Thus, since the contact angle of the liquid Zn droplet on a steel substrate decreases, accompanied by certain spread-wetting and alloying reactions, we cannot determine an exact equilibrium contact angle. However, it was reported¹²⁾ that the contact angle was recognized to be an equilibrium contact angle for about 0.001 s after dropping a droplet on the substrate, in which the droplet and the substrate are known not to react with each other. Therefore, the contact angle of a droplet on a substrate observed during the vibration period just after dropping the droplet can be regarded as an equilibrium contact angle before the alloying reaction occurs. In the present work, we considered that the inertia force experienced as a result of the dropping procedure affects the vibration of a droplet for about 0.03 s just after dropping. After that, the contact angle indicates a stable vibration from 0.03 to 0.1 s, as shown in Fig. 4, which means that the contact angle is not affected by the inertia force accompanying the dropping procedure and alloying reactions.

Table 1. Initial contact angles of liquid Zn on low-carbon steel and Si-Mn steel.

| | | Substrates | |
|-----------------------------|---------|------------------|-------------|
| | | Low-carbon steel | Si-Mn steel |
| Initial contact angle | Run 1 | 38 | 78 |
| $\theta_{initial}$ / degree | Run 2 | 42 | 90 |
| | Average | 40 | 84 |

Table 2. Work of adhesion of liquid Zn to low-carbon steel and Si-Mn steel.

| | Substrates | |
|--|------------------|-------------|
| | Low-carbon steel | Si-Mn steel |
| Work of adhesion W_a / mNm ⁻¹ | 1327 | 830 |

Consequently, we defined the average value of the contact angle during the stable vibration for 0.03–0.1 s after dropping to be an initial contact angle $\theta_{initial}$. Strictly speaking, this initial contact angle $\theta_{initial}$ is different from the contact angle for a non-reaction system, but it corresponds to the equilibrium contact angle which is not affected by an alloying reaction. The vibration period just after dropping depends upon the potential and kinetic energies generated from the dropping action, as well as depending upon the wettability and viscosity of the liquid droplet. Therefore, although the vibration period (0.03–0.1 s) obtained in the present work is different from the period reported in Ref. 12), which described that the vibration period is about 0.001 s in length, we consider that the average value of the contact angle from 0.03 to 0.1 s after dropping is an initial contact angle.

Table 1 shows the values of initial contact angles $\theta_{initial}$ of liquid Zn on low-carbon steel and Si-Mn steel sheets. As shown in this table, the contact angle for low-carbon steel is smaller than that for Si-Mn steel sheet, which means that the wettability for low carbon steel is better than that for Si-Mn steels. From the contact angle measurements, it is possible to evaluate the work of adhesion W_a from Young's equation in Eq. (1) and the definition of the work of adhesion in Eq. (2). In other words, when we substitute σ_s in Eq. (1) into the first term on the right-hand side of Eq. (2), the work of adhesion W_s can be expressed by the surface tension of liquid σ_l and the contact angle θ as shown in Eq. (3).

$$\sigma_s = \sigma_l + \sigma_i \cdot \cos \theta \dots \dots \dots (1)$$

$$W_a = \sigma_s + \sigma_l - \sigma_i \dots \dots \dots (2)$$

$$= \sigma_l \cdot (1 + \cos \theta) \dots \dots \dots (3)$$

Here, σ_s : surface tension of solid, σ_l : surface tension of liquid, σ_i : interfacial tension between solid and liquid, θ : contact angle. When we insert the values for the surface tension of liquid Zn¹³⁾ and the experimental results of $\theta_{initial}$ into σ_l and θ respectively, the work of adhesion W_a was obtained. The results are shown in Table 2. The larger value of the work of adhesion W_a means the liquid Zn has a better wettability on steel sheets.

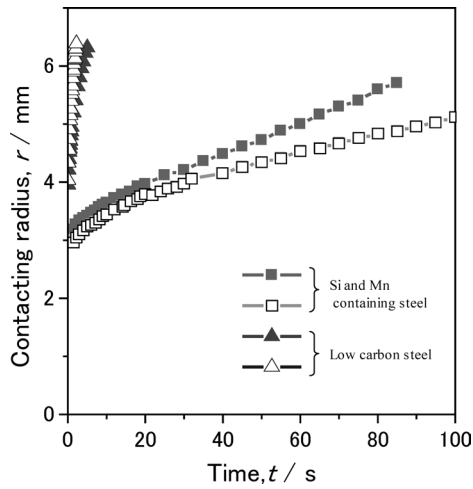


Fig. 6. Change in contacting radius of liquid Zn on low-carbon steel and Si-Mn steel with time.

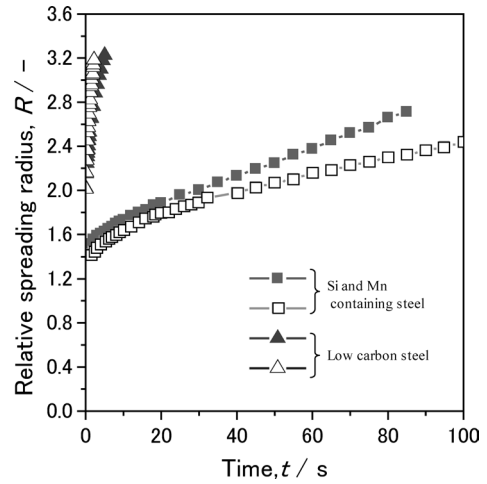


Fig. 7. Change in relative spreading radius of liquid Zn on low-carbon steel and Si-Mn steel with time.

Table 3. Mass of liquid Zn droplet in each experiment.

| | | Substrates | |
|-----------------------|-------|------------------|-------------|
| | | Low-carbon steel | Si-Mn steel |
| Mass of a droplet / g | Run 1 | 0.20 | 0.26 |
| | Run 2 | 0.28 | 0.27 |

3.2. Evaluation of Spreading Velocity

Figure 6 shows the change in radius of a Zn droplet after contacting the substrate with time. Since the radius of the droplet depends on the amount of liquid, we defined a relative spreading radius $R=r/r_{sph}$. Here, r is the radius of the droplet for each experiment, of which the mass of a droplet is shown in Table 3. r_{sph} is the radius of a hypothetical sphere, of which the volume is determined from the mass of a droplet in Table 3 and the density of liquid Zn at 600°C. The change in $R=r/r_{sph}$ with time is shown in Fig. 7. As can be seen in this figure, the relative spreading radius indicates the value of about 1.0 just after dropping and then increases with time. Sometimes, the droplet was observed to spread over the whole surface area of a substrate, which means that the relative spreading radius becomes about 3.2. Over 3.2, it was impossible to measure the radius in the present apparatus.

We defined the differential rate of the relative spreading radius dR/dt to be a relative spreading velocity V . The change in the relative spreading velocity V with time is shown in Fig. 8. Figure 9 shows the change in V with time (100 s) for steel sheets containing Si and Mn. The relative spreading velocity indicates a large value just after dropping the droplet on the steel substrate. Then, the relative spreading velocity decreased gradually and finally became almost constant (for about 20 s), especially for Si-Mn steel sheets, and then the droplet spread at a constant rate. As shown in Fig. 8, the value of the relative spreading velocity for low-carbon steel is larger than that for Si-Mn steel sheets. For low-carbon steel, the relative spreading velocity does not become constant because it spreads very fast and the forefront of the droplet reaches the end of the substrate in only a few seconds.

From the changes in the contact angle and the relative spreading velocity with time, the correlation of the contact

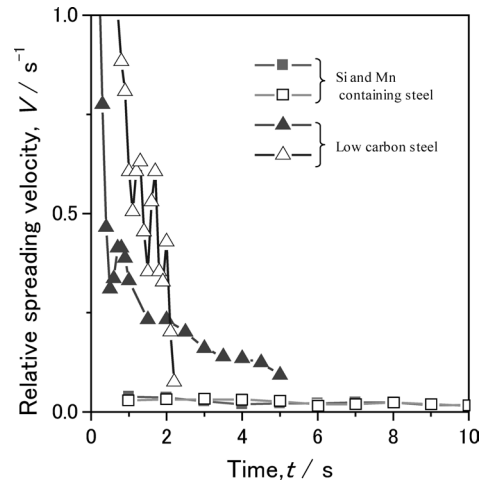


Fig. 8. Change in relative spreading velocity of liquid Zn on low-carbon steel and Si-Mn steel with time.

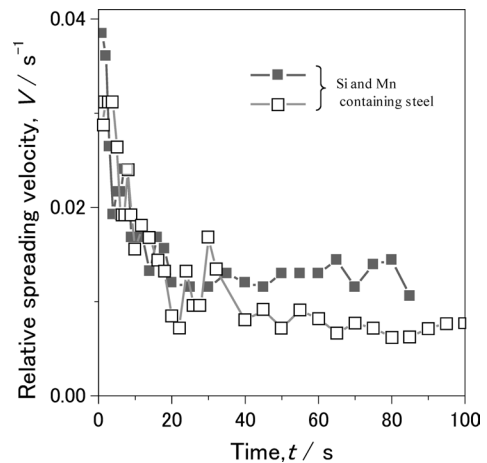


Fig. 9. Change in relative spreading velocity of liquid Zn on Si-Mn steel with time.

angle with the relative spreading velocity can be obtained as shown in Fig. 10. As can be seen in this figure, the contact angle and the relative spreading velocity indicate large values just after dropping but they gradually decrease. In particular, the relative spreading velocity becomes constant against small contact angles for Si-Mn steel sheets. The Zn

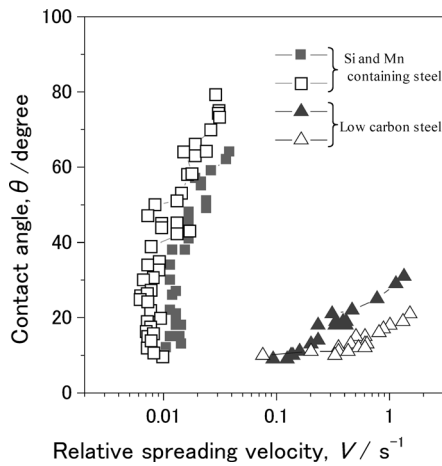


Fig. 10. Relationship between contact angle and relative spreading velocity.

droplet can be affected by various effects such as inertia force, diffusion, alloying reactions, surface tension, interfacial tension and so on. Just after dropping the droplet on the substrate, the contact angle changes drastically with time while keeping the inertia force and maintaining the balance among the surface tensions of liquid Zn and solid steel as well as the interfacial tension between liquid Zn and the solid substrate. However, at the final stage of the spreading, the effect of the inertia force disappears and the contact angle changes with time in a steady state keeping the balance of the surface tensions and the interfacial tensions among liquid Zn, solid steel and metallic compounds which forms gradually due to alloying reactions. That is to say, after the contact angle becomes small and constant, the relative spreading velocity indicates the apparent wettability of liquid Zn on steel sheets which is caused by alloying reactions. In the present work, although the contact angle for low-carbon steel does not indicate a constant value, we can evaluate the wettability based on spread-wetting and alloying reactions by comparing the relative spreading velocity for Si–Mn steel sheets with that for low-carbon steel when the contact angle becomes as small as possible. However, when the contact angle is equal to 10° , the droplet reaches the end of the substrate, such that we cannot measure the contact angle exactly for low-carbon steel. Consequently, we compared the relative spreading velocity against $10\text{--}30^\circ$ of the contact angle for two kinds of the substrates, the results of which are shown in **Table 4**. As shown in this table, the spreading wettability of low-carbon steel is evaluated to be 10–100 times better than that for Si–Mn steel sheets when the contact angle becomes $10\text{--}30^\circ$.

Table 4. Relative spreading velocity at 30 degrees of contact angle of liquid Zn on low-carbon steel and Si–Mn steel.

| | | Substrates | |
|--|---------|------------------|-------------|
| | | Low-carbon steel | Si–Mn steel |
| Relative spreading velocity V / s^{-1} | Run 1 | 1.0 | 0.010 |
| | Run 2 | 1.1 | 0.008 |
| | Average | 1.1 | 0.009 |

4. Concluding Remarks

We were able to quantitatively evaluate the wettability of liquid Zn on low-carbon steel and Si–Mn steel sheets from observations of the dynamic wetting behavior by the sessile drop method. The results obtained are as follows:

- (1) The wettability can be evaluated by measuring the contact angle of the liquid Zn droplet just after the droplet contacted the substrate surface. The initial contact angle was defined as the average value of the contact angle which vibrated for a while just after being dropped. From the work of adhesion obtained from the initial contact angle, the wettability of liquid Zn for Si–Mn steel sheets is evaluated to be worse than that for low-carbon steel.
- (2) The relative spreading radius and the relative spreading velocity were obtained from the change in the apparent radius of the droplet with time when the droplet spread on the substrate. By measuring the relative spreading velocity against the small contact angle at the final stage of spreading, the spreading wettability of liquid Zn for Si–Mn steel sheets was evaluated to be worse than that for low-carbon steel.

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