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Evaluation of Dynamic Wettability of Liquid Zn with Steel Sheets Containing Si and Mn

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It is pointed out that non-wetting behavior of liquid Zn alloy occurs on high-tensile strength steels, which usually contain Si and Mn. There have been a lot of investigations to improve the above wettability of liquid Zn alloy with steels containing Si and Mn. Although those studies evaluated the wettability qualitatively by observation of the surface of steels galvanized by Zn or exfoliation test of Zn with substrate steels and so on, it is required to evaluate the wettability of liquid Zn with steels by measuring contact angle, work of adhesion, spreading velocity etc. which are usually used to assessment of general wetting behavior. In the present work, we evaluated the wettability of liquid Zn with steels containing Si and Mn by applying a sessile drop method to measure the change in contact angle and diameter of liquid Zn droplet wetted on steels.

Keywords *: wettability, contact angle, galvanizing, corrosion, tensile strength*

1. Introduction

Galvanizing of liquid Zn to steel has been widely used for protection of corrosions in steels for automobiles, home electric appliances, buildings and so on.[1),2)] In particular, alloying galvanizing is usually applied to steels for automobiles because of its highly preventing corrosion and good pressing deformation etc.[1),2)] On the other hand, high tensile strength steels have been developed for automobile industries to improve fuel consumption and safety issues etc. There are various high tensile strength steels, such as TRIP steels (Transformation Induced Plasticity steels), Dual Phase steels, Bake Hardening steels etc. which satisfy some required properties on high strength and good deformation quality.[2)] The high tensile strength steels usually contain Si and Mn.

For those galvanizing procedures, it has been known that several bad wetting behaviors occur for high-tensile strength steels containing Si and Mn.[3)] It has been pointed out that one of the reasons for the bad-wettability for high-tensile strength steels is related to the formation of oxides of Si and Mn on steel surface. In order to cope with 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.[4)-19)]

For the wettability of liquid Zn to steels, there have been some qualitative evaluations after galvanizing processing, such as counting the number of defects with bad-wetting,[11),12)] or measuring the mechanical adhesion properties of Zn layer with steel substrates etc. These methods are useful from the technical view points, but it is difficult to evaluate the wetting itself, in other words, the wetting behavior of liquid Zn to steel substrates during galvanizing processing from in-situ observations. As general observation and evaluation methods for the wetting, the sessile drop method has been used widely.[20)] When the contact angle is smaller than 90°, we call the situation to be wetting. In addition, it is possible to evaluate quantitatively the wettability from the work of adhesion,[21)] which can be evaluated from the contact angle. However, when liquid Zn reacts with solid steel substrate to form metallic compounds because of their mutual solubility, the liquid Zn spreads on the surface of solid steel substrates on the basis of alloying reaction as a driving force. Since the contact angle changes with the alloying reactions, it is impossible to measure the equilibrium contact angle of a liquid Zn droplet with steel substrates.

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In the present paper, our recent trials[18),19)] are described on the quantitative evaluation of 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. In our evaluation, we defined the following two quantitative properties: (1) 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. (2) 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. On the basis of the above quantitative evaluation of the dynamic wetting, we compared the wetting behavior of liquid Zn on Si & Mn steels with that on low carbon steels.

2. Experimental[18),19)]

In the present work, the wetting experiments were carried out for low-carbon steel (Fe-0.13mass%Mn) and steels containing Si and Mn (Fe-1.0mass%Si-1.0mass%Mn : Si & Mn steel). These specimens were prepared in a vacuum melting furnace. After the specimens were hot-rolled and then cold-rolled, a specimen with 1 mm × 20 mm × 20 mm was prepared as a substrate. In order to remove oxides from the surface of the specimen, the specimen was polished using emery paper and alumina powder, and finally dried after 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. 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 mmφat the bottom of the crucible, through which a liquid Zn droplet 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 H_2 gas, and the specimen and substrate heated up to 600 ℃. After keeping the specimen for 30 min at 600 ℃, a Zn droplet was 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 ℃) and the atmosphere (H_2 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 on the surface of the small Zn droplets to establish a method to quantitatively evaluate the

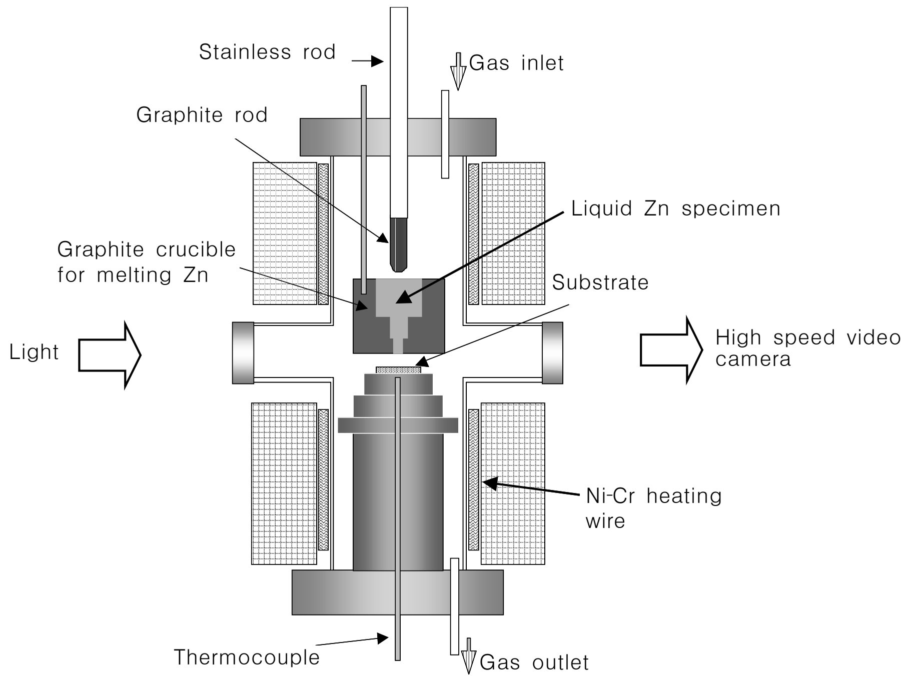

Fig. 1. Schematic diagram of experimental apparatus for sessile drop method.

wetting behavior of liquid Zn on Si & Mn steel sheets.

3. Experimental results and discussion

3.1 Evaluation of contact angle[18),19)]

Fig. 2 represents one example of the spreading behavior of a Zn droplet on a Si & Mn steels. The droplet was dropped from the crucible which was set 6 mm above the substrate. Fig. 3 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. 4 from the time 0.1 sec after dropping the droplet until the contact angle become less than 10°. These two figures correspond to the experimental results obtained for two kinds of specimens, that is to say, low-carbon steel and Si & Mn steels. As shown in these figures, the contact angle decreases with time, and finally falls below 10º. Figs. 3 and 4 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. 3, during the vibration of the droplet, of which the amplitude was almost constant, the contacting area between the droplet and the substrate increased and decreased repeatedly. We considered that the inertia force as a result of the dropping action affects the vibration of a droplet for about 0.03 sec just after dropping. It is confirmed that the contact angle changes periodically from 0.03 to 0.1 sec just after dropping while the contact area of the droplet with steel substrates increases and decreases

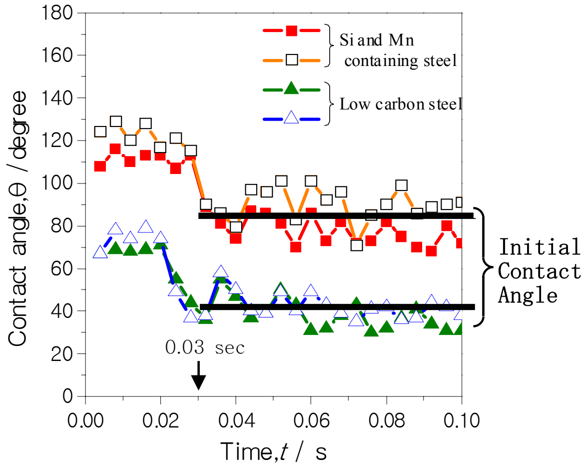

Fig. 3. Determination of initial contact angle of liquid Zn on low carbon steel and Si & Mn steel.

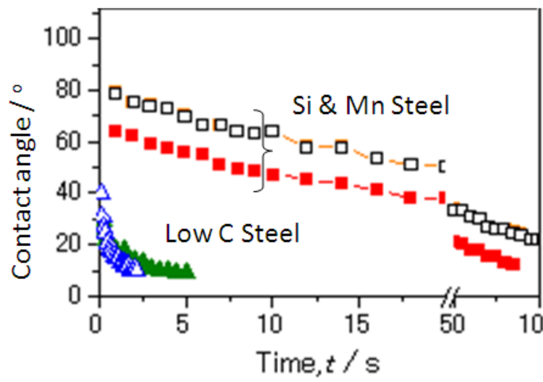

Fig. 4. Change in contact angle of liquid Zn droplet on low carbon steel and Si & Mn steel with time.

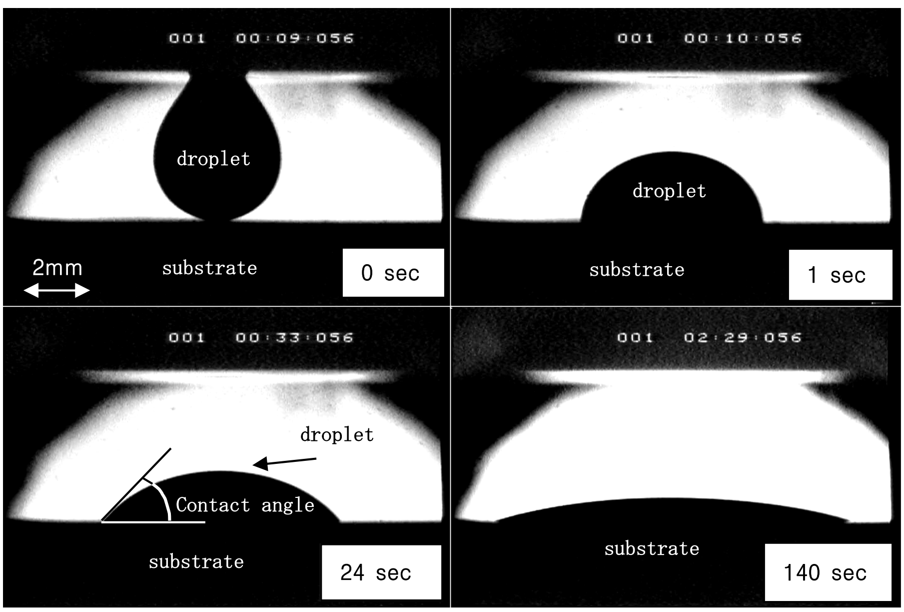

Fig. 2. Change in droplet shape of liquid Zn on Si & Mn steel substrate with time.

repeatedly. This behavior indicates that any alloying reaction does not occur between Zn droplet and steel substrate. Once metallic compounds form at the interface, it is supposed that the contact angle decreases gradually without any return to the initial value. Thus, the wettability of a Zn droplet with steel substrate just after dropping is not affected by alloying reactions. Consequently, the average value of the contact angle, which vibrate periodically just after dropping, is defined as 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.

As shown in Fig. 3, the values of initial contact angles $\theta_{initial}$ of liquid Zn on 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).

$$\sigma_s = \sigma_i + \sigma_l \cdot \cos\theta \tag{1}$$

$$W_a = \sigma_s + \sigma_l - \sigma_i = \sigma_l \cdot (1 + \cos\theta) \tag{2}$$

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 Zn[22] and the experimental results of $\theta_{initial}$ into σ_l and θ respectively, the work of adhesion W_a can be obtained. As indicated in Eq.(2), the smaller value of the contact angles means the larger value of the work of adhesion when σ_l is common, and the larger value of the work of adhesion W_a corresponds to the liquid Zn has a better wettability on steel sheets.

3.2 Evaluation of spreading velocity[18),19)]

The change in radius of a Zn droplet after contacting the substrate with time was also measured in the present work. 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 was measured after the experiments. r_{sph} is the radius of a hypothetical sphere, of which the volume is determined from the mass of a droplet and the density of liquid Zn at 600℃.[22)] The change in $R = r / r_{sph}$ with time is shown in Fig. 5. As can be seen in this figure, the relative spreading radius for low carbon steel increases more rapidly than that for Si & Mn steels. This means that liquid Zn wets better with low carbon steel sheets compared for Si & Mn steels.

The differential rate of the relative spreading radius dR/dt is defined to be a relative spreading velocity V. The change in the relative spreading velocity V with time is shown in Fig. 6. Fig. 7 shows the change in V with time (100 sec) for Si & Mn steel sheets because it is difficult to see the change of V with time for Si & Mn Steels in Fig. 6. The relative spreading velocity indicates a large value just after dropping the droplet on the steel substrate. Then, the value of V decreased gradually and finally became almost constant (for about 20 sec), especially for

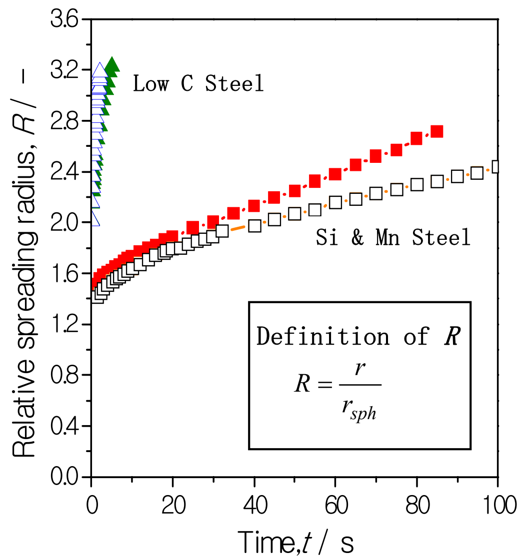

Fig. 5. Change in relative spreading radius R of liquid Zn droplet on low carbon steel and Si & Mn steel with time.

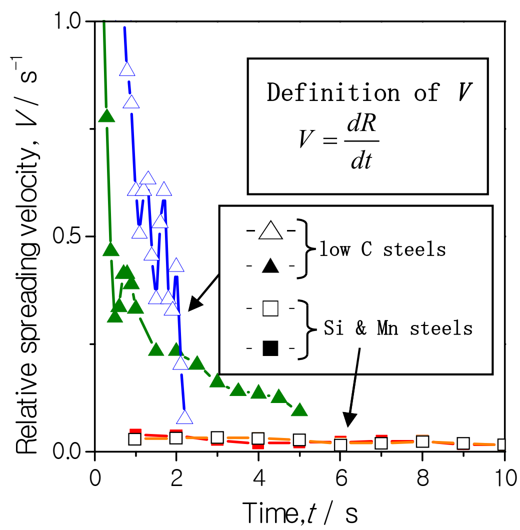

Fig. 6. Comparison of the change in V against time for low carbon steel with that for Si & Mn steel.

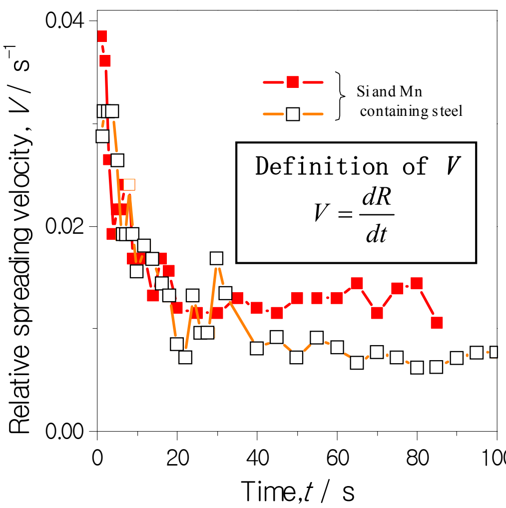

Fig. 7. Change in relative velocity V of liquid Zn droplet on Si & Mn steel with time.

Si & Mn steel sheets, and then the droplet spread at a constant rate. As shown in Fig. 6, 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. Thus, from the observation of the relative spreading radius and the relative spreading velocity, we can evaluate the dynamic wetting behavior, and it is found clearly that liquid Zn wets better on low carbon steel than on Si & Mn steels. The above procedure can be applied to investigate the wettability of liquid Zn with steel sheets containing various amounts of Si and Mn.

4. Conclusions

It is possible to evaluate the wettability of liquid Zn on low-carbon steel and Si & Mn steel sheets from the observations of 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 initial contact angle obtained from the present work, 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. From the above information, the spreading wettability of liquid Zn for Si & Mn steel sheets was evaluated to be worse than that for low-carbon steel.

3) The above procedures can be applied to the evaluation of wettability of liquid Zn with high tensile strength steels containing various concentrations of Si and Mn.

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References

1. *Handbook of Galvanizing*, (ed. ISIJ) (1999).
2. Nippon Steel, *Visual Engineering Book on Iron and Steel*, Nihon Jitsugyou Publishing (2004).
3. Y. Hirose, H. Togawa, and J. Sumitani, *Tetsu-to-Hagane*, **68**, 665 (1982).
4. Y. Tsuchiya, T. Hashimoto, Y. Ishibashi, J. Inagaki, and Y. Fukuda, *Tetsu-to-Hagane*, 86, 396 (2000).
5. Y. Tobiyama and C. Kato, *Tetsu-to-Hagane*, 89, 38 (2003).
6. I. Hashimoto, K. Saitou, M. Nomura, T. Yamamoto, and H. Takeda, *Tetsu-to-Hagane*, 89, 31 (2003).
7. N. Fujibayashi, K. Kyouno, and C. Kato, *Tetsu-to-Hagane*, **89**, 23 (2003).
8. Y. Hirose, H. Togawa, and J. Sumiya, *Tetsu-to-Hagane*, **68**, 2551 (1982).
9. A. Komatsu, A. Andou, and T. Kittaka, *Nisshin Steel Tech. Rep.*, **77**, 1 (1998).
10. Y. Takada, M. Suehiro, M. Sugiyama, K. Honda, and A. Itami, *Shin-nitetsu Giho*, **381**, 66 (2004).
11. Y. Suzuki, Y. Tobiyama, and C. Kato, *CAMP-ISIJ*, **13**, 591 (2000).
12. Y. Suzuki, K. Kyono, and C. Kato, *CAMP-ISIJ*, **15**, 1123 (2002)
13. C. Kato, T. Sekine, S. Umino, T. Yamashita, K. Mochiduki, and M. Masuda, *CAMP-ISIJ*, **7**, 1511 (1994).
14. K. Nishimura, T. Odashima, and Y. Hirano, *CAMP-ISIJ*, **12**, 551 (1999).
15. N. Ebrill, Y. Durandet, and L. Strezov, *Metall. Mater. Trans. B*, **31B**, 1069 (2000).
16. Y.Chung, J.Wang, and J.M.Toguri, *IRON & STEELMAKER*, JULY, 6 (2001).
17. S. Hara and H. Asano, *CAMP-ISIJ*, **5**, 1737 (1992).
18. S. Shimada, Y. Takada, J.Lee, and T. Tanaka, *ISIJ Int.*, **48**, 1246 (2008).
19. Y. Takada, S. Shimada, J. Lee, M. Kurosaki, and T. Tanaka, *ISIJ Int.*, **49**, 100 (2009).
20. A.I. Rusanov and V.A. Prokhorov, *Interfacial Tensiomentry*, Elsevier, New York, 84 (1996).
21. A.W. Adamson, *Physical Chemistry of Surfaces*, John Wiley & Sons, New York, 424 (1982).
22. T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, (1988).