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Citation	ISIJ International. 2009, 49(1), p. 100-104
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/26381">https://hdl.handle.net/11094/26381</a>
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# The Effect of Si and Mn Content on Dynamic Wetting of Steel with Liquid Zn

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(Received on July 30, 2008; accepted on October 10, 2008; originally published in *Tetsu-to-Hagané*, Vol. 93, 2007, No. 8, pp. 532–537)

Non-wetting behavior of liquid Zn alloy sometimes occurs on high-tensile strength steels that usually contain Si and Mn. Many studies have been undertaken to improve the wettability of liquid Zn. In this work, we applied the 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. We could then quantitatively evaluate the wettability of those steels using liquid Zn. Si weakens the work of adhesion and spreading velocity of liquid Zn on steels. Mn, however, has a small effect on the contact angle and the work of adhesion but occasionally increases the spreading velocity even when Si content is high in steels.

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

## 1. Introduction

Hot dip Zn galvanizing to steel is a widely used method for corrosion protection in automobile steel, home electric appliances, buildings *etc.*<sup>1,2)</sup> In particular, galvannealing is used for automobile steel as corrosion is prevented and the alloys have good pressing deformation properties.<sup>1,2)</sup> High tensile strength steels have, however, been developed for the automobile industries to improve fuel consumption and to improve safety. There are various high tensile strength steels such as TRIP steels (Transformation Induced Plasticity steels), dual phase steels and bake hardening steels *etc.*, which satisfy some required properties such as high strength and good deformation ability.<sup>2)</sup> High tensile strength steels usually contain Si and Mn. It is known that non-wetting behavior of liquid Zn alloy occasionally occurs on high-tensile strength steels.<sup>3)</sup> One of the reasons for the bad wettability associated with high tensile strength steels is that selective oxidation of Si and Mn on the steel surface. Many reports have focused on the wettability of liquid Zn on steels containing Si and Mn.<sup>4–14)</sup> The wettability of liquid Zn on steels has been reported to improve upon addition of Ni to the liquid Zn bath<sup>10)</sup> or by oxidation and reduction processing<sup>9)</sup> *etc.*

The wettability of liquid Zn on steels has been qualitatively evaluated after galvanizing processing by counting the number of defects with bad-wetting<sup>11,12)</sup> or measuring the mechanical adhesion properties of a Zn layer with steel substrates. These methods are technically useful but it is

difficult to evaluate the specific wetting property, which is the wetting behavior of liquid Zn on steel substrates during galvanizing processing. The sessile drop method has been widely used as a general observation and evaluation method for wetting.<sup>15)</sup> The equilibrium contact angle of a liquid droplet on a solid substrate, if no reaction takes place, is determined from the balance of the surface tension of a liquid droplet with that of a solid substrate and the interfacial tension of the solid–liquid interface. Wetting refers to the situation where the contact angle is less than 90°. It is possible to quantitatively evaluate the wettability from the work of adhesion,<sup>16)</sup> which may be obtained from the contact angle. When liquid Zn reacts with solid steel to form metallic compounds, due to their mutual solubility, the liquid Zn spreads on the surface of the solid steel and the alloying reaction is a driving force. Since the contact angle changes during the alloying reactions, it is difficult to measure the equilibrium contact angle of a liquid Zn droplet with steel substrates. No methods have been established to quantitatively evaluate the dynamic wetting behavior of liquid Zn on steel substrates of various chemical compositions. A few reports have addressed the change in contact angle of a liquid Zn droplet on a steel substrate by the sessile drop method.<sup>17–19)</sup>

In our previous work,<sup>20,21)</sup> a high speed camera was used to observe the spreading behavior of a liquid Zn droplet, just after the droplet attached on a solid steel substrate, as a change in the contact angle. We defined the contact angle of liquid Zn with the steel substrate just after dropping the

droplet as the initial contact angle before the alloying reaction, which corresponded to the equilibrium contact angle. Since the spreading of the droplet on the substrate with a small contact angle is driven by alloying reactions, we evaluated the wettability by using the spreading velocity of the droplet. We have thus shown<sup>20,21)</sup> that it is possible to evaluate the wettability of Si–Mn added base steel from *in-situ* observations of liquid Zn droplet behavior.

The purpose of the present work is to investigate the effect of Si and Mn content in steels on the dynamic wettability of liquid Zn with Si–Mn added steels by applying the experimental procedures discussed above.

## 2. Experimental

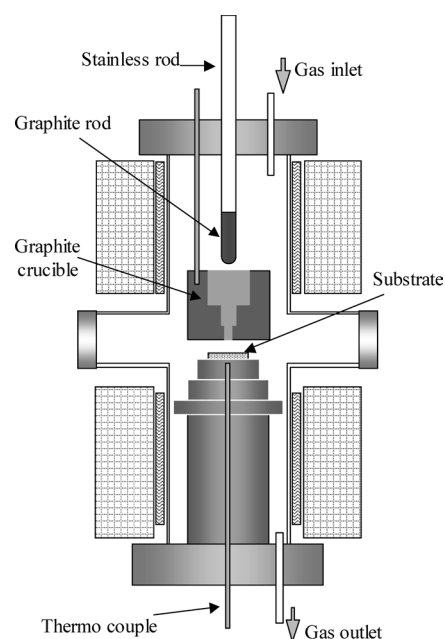
The wetting experiments were carried out on the steels with chemical compositions of Si and Mn as listed in **Table 1**. These specimens were prepared in a vacuum melting furnace. After the specimens were hot-rolled (Soaking Temp.: 1230°C, Finishing Temp.: 900°C, Coiling Temp.: 720°C) and then cold-rolled (4.0 mm→1.0 mm) a specimen with 1 mm×20 mm×20 mm was prepared as a substrate. To remove the oxides from the surface of the specimen it was polished using emery paper #1 500 as well as alumina powder and finally dried after the oil had been removed from the surface. A schematic diagram of the experimental apparatus for the wetting observations is shown in **Fig. 1**. The specimen, as a substrate, is mounted on a graphite support stand in the center of the furnace and a graphite crucible for melting Zn is placed above the substrate. A hole with a diameter of 1.5 mm at the bottom of the crucible allows liquid Zn droplets to be dropped from the crucible onto the substrate beneath. 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 a Zn specimen, the atmosphere in the furnace was replaced by H<sub>2</sub> gas. The specimen and substrate were then heated to 600°C according to the profile shown in **Fig. 2**. After 30 min at 600°C a Zn droplet was then deposited onto the substrate. The temperature of the crucible and the substrate can be controlled individually from two independent heating elements made of Ni–Cr wires. The temperature (600°C) and the atmosphere (H<sub>2</sub> gas) were selected, after several trials, to form some typical oxides of Si or Mn on the surface of substrates as well as to prevent the formation of oxides on the surface of liquid Zn droplet. These experimental conditions are different from the conventional industrial conditions but the prevention of surface oxide formation on the surface of the Zn droplets is necessary. A method for the quantitative evaluation of the wetting behavior of liquid Zn on steel sheets containing Si and Mn may thus be established. The change of the shape of a Zn droplet was observed by a video camera, by which 250 frames per second can be taken. The changes in the contact angle  $\theta$  of the droplet on a steel substrate and the droplet radius  $r$  with time were measured from those pictures.

## 3. Experimental Results

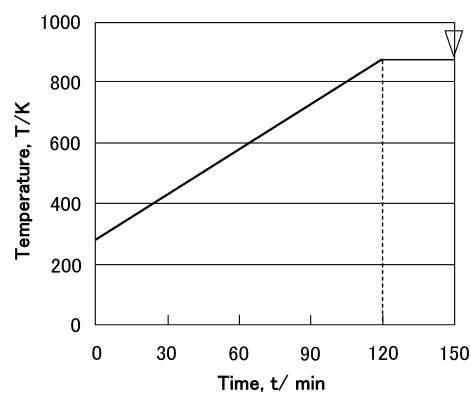
**Figure 3** represents an example of the spreading behavior of a liquid Zn droplet on a steel substrate

**Table 1.** Chemical composition of Si–Mn steels.

	C	Si	Mn	Al	P	S
Sub. 01	0.05	0.01	0.5	0.03	0.01	0.002
Sub. 02		0.50				
Sub. 03		1.00				
Sub. 04		1.50				
Sub. 05		0.01	1.0			
Sub. 06		0.50				
Sub. 07		1.00				
Sub. 08		1.50				
Sub. 09		0.01	1.5			
Sub. 10		0.50				
Sub. 11		1.00				
Sub. 12		1.50				
Sub. 13		0.01	2.0			
Sub. 14		0.50				
Sub. 15		1.00				
Sub. 16		1.50				



**Fig. 1.** Schematic diagram of the experimental set-up for the sessile drop method.



**Fig. 2.** Temperature profile of the experiment.

(1.0mass%Si–1.0mass%Mn: Sub.07) under a H<sub>2</sub> atmosphere. The contact angle of the droplet changes periodically due to vibration just after dropping but this effect decreases gradually with time. As the spreading proceeds with time, the spreading radius  $r$  increases and the contact angle de-

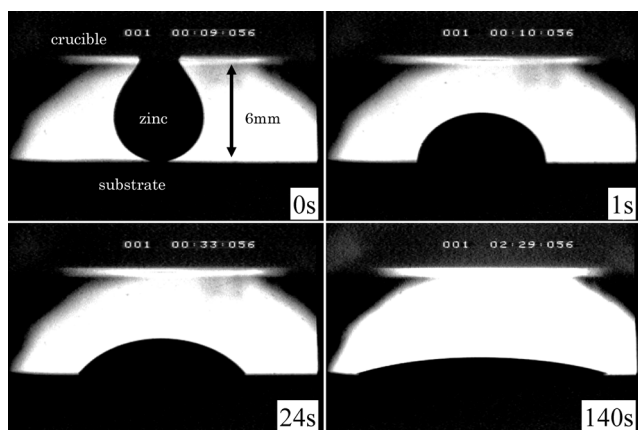


Fig. 3. Change in droplet shape of liquid Zn on the steel sheet of 1.0mass%Si-1.0mass%Mn.

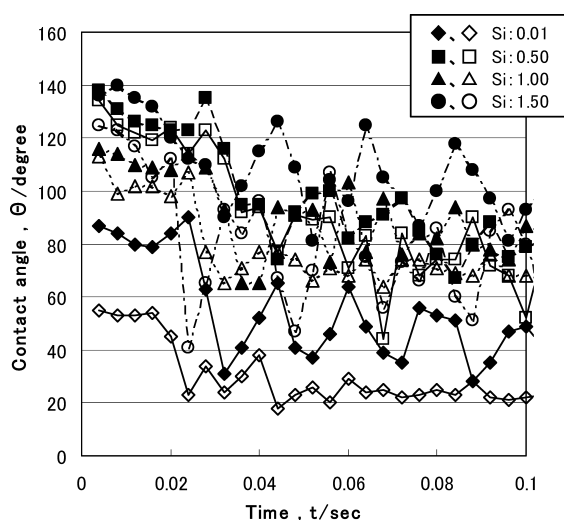


Fig. 4. Change in the initial contact angle of liquid Zn on various Si-1.0mass%Mn steels with time.

creases with accompanying alloying reaction.

Figure 4 shows the change in the contact angle, within the initial 0.1 s of a droplet of liquid Zn on steel substrates containing 1 mass% Mn with different Si contents. Figure 5 shows the change in the contact angle of a droplet of liquid Zn with time, until the contact angle is less than 20°. Duplicate results for the same steel, obtained from two different experiments, are shown in Figs. 4 and 5. These results indicate that the uncertainty of the experimental results for the contact angle is about 10° for the same steel. The droplets vibrate just after dropping but the contact angle decreases with time. As the Si content is increased the contact angle of the droplets, just after dropping, increases and the rate of contact angle decrease is reduced although the results are scattered to some extent.

## 4. Discussion

### 4.1. Initial Wettability of Liquid Zn to Steel without Any Alloying Reactions

The contact angle changes periodically from 0.03 to 0.10 s just after dropping while the contact area of the droplet on the steel substrates increases and decreases repeatedly. This behavior indicates that the alloying reaction does not occur between the Zn droplet and the steel sub-

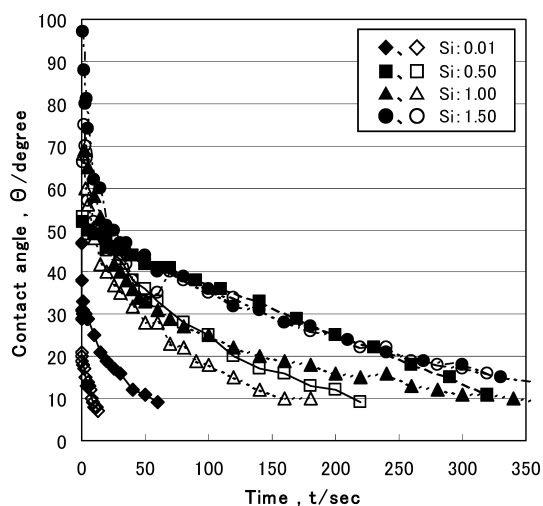


Fig. 5. Change in contact angle of liquid Zn on various Si-1.0mass%Mn steels with time.

strate. If metallic compounds were to form at the interface, the contact angle would decrease gradually without any reversion. The wettability of a Zn droplet with the steel substrates, just after dropping, is not affected by any alloying reactions. The contact angle vibrates just after dropping and thus an average contact angle value is defined as the initial contact angle ( $\theta_{\text{initial}}$ ). The  $\theta_{\text{initial}}$  is different to the contact angle for a non-reactive system but corresponds to an equilibrium contact angle which is not affected by an alloying reaction. The  $\theta_{\text{initial}}$  obtained for each wettability experiment is shown in Fig. 6 and shows the average value of the  $\theta_{\text{initial}}$  obtained twice for each specimen with different chemical compositions. The  $\theta_{\text{initial}}$  increased with increasing Si content in the substrates. The effect of Mn on the  $\theta_{\text{initial}}$  is unclear.

It is possible to evaluate the work of adhesion ( $W_a$ ) using the following Eq. (2) obtained from Young's equation, Eq. (1), for 3 kinds of interfacial tension by using the  $\theta_{\text{initial}}$  values obtained above.<sup>16)</sup>

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

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

Here  $\sigma_s$  is the surface tension of the solid,  $\sigma_l$  the surface tension of the liquid,  $\sigma_i$  the interfacial tension between solid and liquid and  $\theta$  the contact angle. When we insert the values for the surface tension of liquid Zn<sup>13)</sup> and the experimental results of  $\theta_{\text{initial}}$  into  $\sigma_i$  and  $\theta$  into Eq. (2),  $W_a$  was obtained. Figure 7 shows the equi-work of adhesion curves with the respective Si and Mn content of the steel substrates. The values in Fig. 7 indicate the average value of  $W_a$  obtained twice for each specimen with different chemical compositions. It is supposed that liquid Zn adheres strongly to steels, in other words, liquid Zn wets well with steel substrates immersed in liquid Zn during galvanizing processing as the value for  $W_a$  increases. Figure 7 shows that the wettability of liquid Zn with steel substrates becomes worse with increasing Si content and the effect of Mn on the wettability is not clear. Good values for wettability are obtained at 1.0 mass% Mn and 2.0 mass% Mn, even with high Si content. Kato *et al.*<sup>13)</sup> have reported good wettability at 0.5–1.0 mass% Mn and 0.5 mass% Si, which was

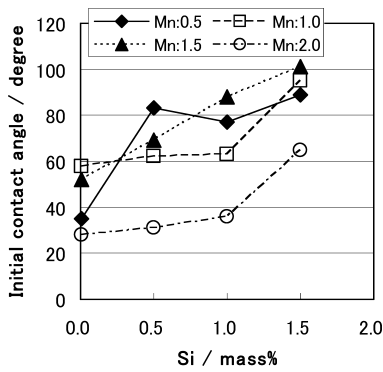


Fig. 6. Initial contact angle of liquid Zn on various Si-Mn steels.

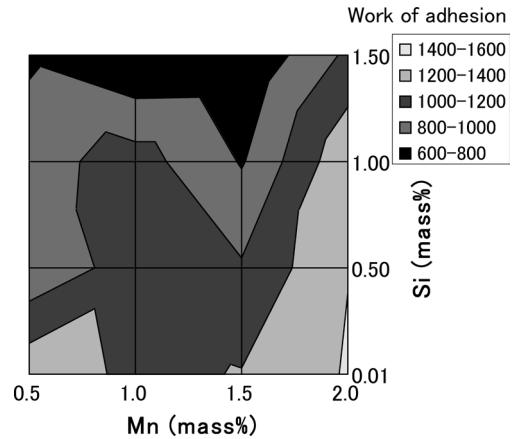
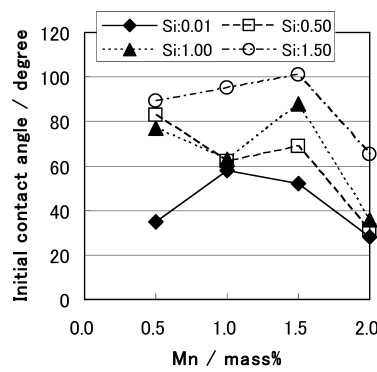


Fig. 7. Work of adhesion of liquid Zn on various Si-Mn steels.

due to the change in the form of oxides in practical galvanizing processing. A comparison of our results to that of Kato *et al.*<sup>13)</sup> reveals similar wettability at 1.0 mass% Mn with high Si content but reveals different results for 2.0 mass% Mn with high Si content. The atmosphere in our work was different to the atmosphere in their work<sup>13)</sup> and thus the formation of oxides on the steel substrates could be different each other.

#### 4.2. Wettability of Liquid Zn with Steel during Alloying Reactions

Just after dropping, the contact angle changes periodically from 0.03 to 0.10 s. The contact angle then decreases gradually. This wetting behavior is driven by alloying reactions of liquid Zn with the steel substrate. **Figure 8** shows the change in the relative spreading radius  $R$  with time for substrates with various Si content and with 1.0 mass% Mn in the steel substrates. The relative spreading radius  $R$  has been defined in our previous work<sup>20,21)</sup> as follows:

$$R = r/r_{\text{sph}} \dots \dots \dots (3)$$

In Eq. (3),  $r$  is the radius of a droplet spread on a steel substrate.  $r_{\text{sph}}$  is the radius of a hypothetical sphere with a volume determined from the density<sup>22)</sup> of liquid Zn at 600°C and the mass of a droplet obtained from the difference between the total mass of Zn spread on a steel substrate and the mass of the substrate before the experiment.

Duplicate results from two different experimental runs are shown in Fig. 8. The relative spreading radius, as shown in this figure, has a value of about 1.0 just after dropping and this increases with time. With greater Si content in steel substrates, the time required to obtain a specific  $R$  value increases and the gradient of the change in  $R$  with time decreases. Since the droplet was occasionally observed to spread over the whole surface area of a substrate, which meant that the relative spreading radius  $R$  reaches a value of about 3, it was impossible to measure the radius of a droplet in the present apparatus with  $R > 3$ .

We defined the differential rate of the relative spreading radius  $dR/dt$  to be the relative spreading velocity ( $V$ ). The change in  $V$  with time is shown in **Fig. 9** for various Si content steels with 1 mass% Mn. Duplicates obtained in two different experimental runs are shown in Fig. 9.  $V$  is large just after dropping a droplet onto the steel substrates.  $V$  then decreases gradually and becomes almost constant. The time taken to reach a final constant value of  $V$  is dependent on the chemical composition of the steel. An increase in the

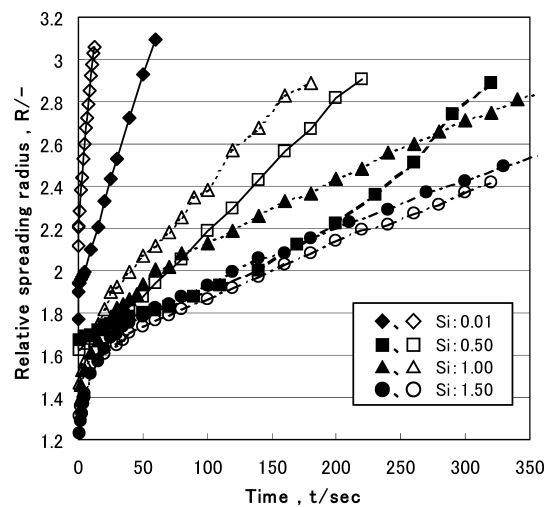


Fig. 8. Change in the relative spreading radius of liquid Zn on various Si-1.0mass%Mn steels with time.

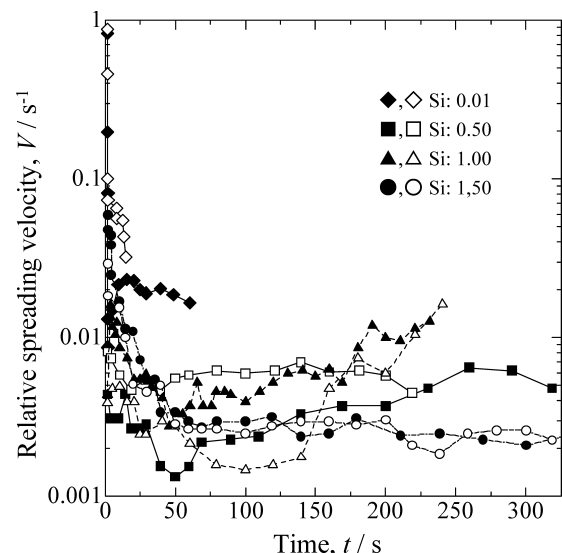


Fig. 9. Change in the relative spreading velocity of liquid Zn on various Si-1.0mass%Mn steels with time.

amount of Si content in steels results in a decrease in  $V$ . We tried to evaluate the effect of Si and Mn content on the wettability during the alloying reactions using  $V$ .

From the changes in the contact angle and  $V$  with time, a



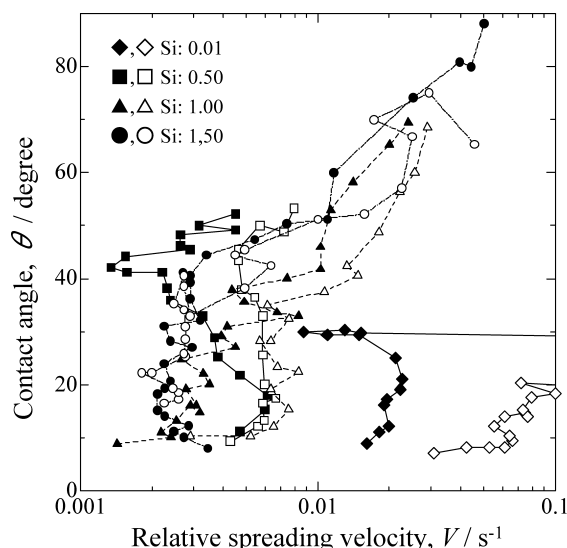


Fig. 10. Relationship between contact angle and relative spreading velocity on various Si-1.0mass%Mn steels.

correlation was obtained and is shown in Fig. 10. Duplicate results were obtained in two different experimental runs and are shown in Fig. 10. The contact angle and  $V$  have large values just after dropping and these gradually decrease.  $V$  has an almost constant final value when the contact angle is  $10^{\circ}$ – $30^{\circ}$ . The Zn droplet can be affected by factors such as inertia force, diffusion, alloying reactions, surface tension, interfacial tension *etc.* Just after dropping the droplet on the substrate, the contact angle changes drastically with time while keeping the inertia force. The balance between the surface tension of liquid Zn and solid steel as well as the interfacial tension is also maintained. At the final stage of droplet spreading, the inertia force disappears and the contact angle changes with time in a steady state. This keeps the balance of surface tension and interfacial tension among liquid Zn, solid steel and metallic compounds formed due to the alloying reactions. When the contact angle becomes small and constant, the relative spreading velocity indicates the apparent wettability of liquid Zn on steel sheets caused by the alloying reactions.<sup>20,21</sup> In this work we have evaluated the effect of Si and Mn content on wettability based on spread-wetting due to alloying reactions when the contact angle is equal to  $20^{\circ}$ . Figure 11 shows the equi-relative spreading velocity at a contact angle of  $20^{\circ}$  with Si and Mn content. The values in Fig. 11 are the averages of the relative spreading velocity obtained twice for each specimen with different chemical compositions. The wettability due to alloying reactions becomes worse as the Si content increases. The wettability due to the alloying reaction, however, improves as Mn content is increased and Si content  $\geq 0.50$  mass%.

## 5. Concluding Remarks

The effects of Si and Mn contents on the wettability of liquid Zn with Si-Mn added steel sheets were evaluated from the observation of the dynamic wetting behavior by the sessile drop method proposed in our earlier work.<sup>20,21</sup>

The results obtained are:

(1) The initial contact angle ( $\theta_{\text{initial}}$ ) was defined as the average value of the contact angle, which vibrated for a

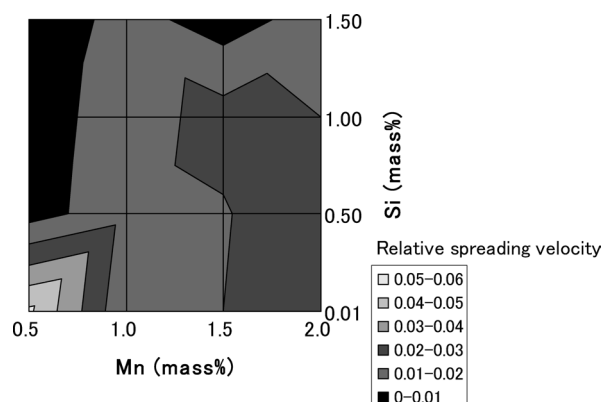


Fig. 11. Relative spreading velocity on various Si-Mn steels.

while just after being dropped. The wettability, without any alloying reactions, can be evaluated by using the work of adhesion obtained from  $\theta_{\text{initial}}$ . Using the current experimental conditions, the wettability of liquid Zn with the steel substrates becomes worse as the Si content increases. The effect of Mn on the wettability is unclear but good wettability is seen at 1.0 mass% Mn and 2.0 mass% Mn even with high Si content.

(2) The wettability during alloying reactions of liquid Zn to Si-Mn steel sheets was evaluated by measuring the relative spreading velocity ( $V$ ) against small contact angles at the final stage of spreading. With increasing Si content, the wettability with alloying reactions becomes worse. Wettability during alloying reactions is, however, improved with an increase in Mn content for Si  $\geq 0.50$  mass%.

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