The Effect of Surface Active Elements on the Wetting Behavior of Iron by Molten Aluminum Alloy

Makoto KOBASHI, Susumu KUNO,¹⁾ Takao CHOH and Takao SHIMIZU²⁾

School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi-ken, 464-01 Japan.

1) Formerly Graduate School, Nagoya University. Now at Department of Body Designing, Mitsubishi Motors Corporation, Nakashingiri, Hashime-cho, Okazaki, Aichi-ken, 444 Japan.

2) Research and Development Division, Daido Steel Co.,

Ltd., Daido-cho, Minami-ku, Nagoya, Aichi-ken, 457 Japan.

(Received on September 26, 1994; accepted in final form on February 17, 1995)

Measurements of the contact angle of molten aluminum alloys (Al–Mg, Al–Cu and Al–Si alloys) on solid iron substrate have been carried out aiming at developing a filler sheet for a welding between iron and aluminum. The wettability was estimated by a sessile drop method. The contact angle of molten aluminum drop was measured at 773 and 893 K. Magnesium alloying decreases the contact angle of molten aluminum drop because an evaporation of magnesium prevents a formation of a thin oxide layer at the surface of the molten drop. Since the vapor pressures of these elements at an experimental temperature are much lower than that of magnesium, neither silicon nor copper alloying contributes to improving a wettability on a given experimental condition ($T=893\text{ K}$, $P=1.33 \times 10^{-3}\text{ Pa}$). A minute quantity of surface active elements such as bismuth, lead and lithium was added with a view to decreasing the surface tension of molten aluminum alloys. A 0.05 mass% addition of bismuth decreases the contact angle most effectively. An excessive addition, however, results in increasing the contact angle. The effect of bismuth addition is more significant at lower temperatures than at higher temperatures.

KEY WORDS: wettability; sessile drop method; aluminum alloy; alloying element; surface activity.

1. Introduction

Steel has been used for centuries and it is used for many kinds of transport vehicles at present. Nevertheless, from the viewpoint of an energy saving, efforts have been made to decrease the weight of such vehicles and a substitution of a light metal like aluminum for steel has begun to be considered. In general, complete substitution of aluminum parts for steel parts is still difficult to achieve, in terms of satisfying strength, reliability, cost and so forth. Hence, a partial substitution is a practical way of an application of aluminum parts, and this requires a bonding between steel and aluminum. Some works relating to a bonding of aluminum with other metals have been carried out by many researchers.^{1–5)} One of the important things here is to achieve a complete contact between two materials in order not to interfere with a heat flow. Brazing using a filler sheet would satisfy this requirement,⁶⁾ if the molten filler spread over the surfaces of both materials. Enjo⁷⁾ has carried out diffusion bonding of aluminum alloy with various materials and also indicated the effectiveness of a presence of molten phase at the interface for obtaining a high bonding strength.

The aim of this work is to develop an aluminum-base filler sheet, which melts below the melting point of pure aluminum and can spread over the iron surface quickly,

for iron/aluminum welding. The contact angle of molten aluminum alloys on a solid iron substrate was measured by sessile drop method. Since the important condition is to achieve a good wettability in a short range of time, the initial contact angle data were mainly focused on. Judging from binary phase diagrams, aluminum–copper, aluminum–magnesium and aluminum–silicon alloys were employed for this experiment because of their low melting points. Surface active elements (bismuth, lead and lithium) were also added aiming at decreasing the surface tension of molten aluminum. In this paper, (1) effects of the surface active elements on the contact angle and (2) temperature dependence of the surface activity of bismuth, lead and lithium are mainly dealt with.

2. Experimental

A pure iron plate (containing less than 0.0015 mass% oxygen and 0.006 mass% nitrogen), 40 mm × 50 mm × 3 mm in size, was used as solid substrate. The surface of the substrate was polished with 3 and 1 μm diamond and 0.05 μm alumina powders in the wet process and then cleaned by ultrasonic rinsing in acetone for 300 s. Since the bonding between aluminum and iron should be carried out at temperatures below a melting point of aluminum, some elements (magnesium, copper and silicon), which form eutectic with aluminum, were added

to aluminum in a range of 10 to 40 mass%. A minute quantity of surface active elements (lead, bismuth and lithium) was also added in order to decrease the surface tension of molten aluminum alloy.

Experimental apparatus, including an infrared furnace and a transparent quartz tube, shown in Fig. 1, was used for a measurement of a contact angle. A graphite plate was placed in a center of the quartz tube and the polished iron substrate was mounted on the carbon plate. Care had been taken to ensure that the iron substrate was horizontal. Approximately 0.2 g of cylindrical aluminum alloy and iron stick, covered with boron nitride, for extruding molten aluminum alloy were inserted in an alumina tube (outer diameter 6 mm, inner diameter 4 mm) with a hole (2 mm) at the tip. The alumina tube and a thermocouple were placed horizontally at a center of the quartz tube. The inside of the quartz tube was evacuated to 1.33×10^{-3} Pa. The whole system was preheated at 573 K and held for 600 s. After preheating, it was heated up to an experimental temperature and held for 300 s. Molten aluminum was pushed out of the tube through the hold and fell onto the substrate 5 mm below. The picture of a drop was taken by a CCD camera and recorded by a video recorder. The contact angle was measured by an image analysis system (PIAS: LA500) from recorded figures. Measurements for the same system on the same condition were carried out at least three times. Inconsistent data were eliminated and measured again to ensure the validity of data. Some figures of a spherical ball and a cubic block was taken by the CCD camera to evaluate the distortion of the recorded figures. The vertical/horizontal aspect ratio of the picture taken by the CCD camera was 1.00, which indicates the distortion caused by the CCD camera was negligible.

An attempt was made to identify the amount of magnesium evaporation during the measurements of the contact angle. In the vacuum chamber, Al-Mg alloy (approximately 0.1 g) was placed on a carbon plate and heated up to both 893 and 773 K and held for 3 to 100 s. A decrease in the magnesium content in the molten drop was estimated by measuring the magnesium content of these specimens with the help of ICP emission spectro-

metric analysis. The relative error of ICP analysis to measure the magnesium content in aluminum was within a few percent.

The average thickness of the reaction layer was measured from the scanning electron micrographs. Twenty lines were drawn perpendicular to the reaction layer and the length of each line overlapping the reaction layer was measured.

3. Results and Discussion

3.1. The Wettability between Iron and Binary Aluminum Alloys

3.1.1. Aluminum-Magnesium System

Three levels of magnesium content of Al-Mg alloy (Al-15, 25, 35 mass%Mg) were employed to investigate how magnesium affects the spreading behavior of molten aluminum on the iron surface. Figure 2 shows the contact angle of Al-Mg drop on the iron substrate at 893 K. The initial contact angle of Al-15mass%Mg drop was about 90° and, after a 60 s holding, the contact angle decreased to 73° . An increase in the contact area between the drop and the iron substrate was also observed. This indicates that the molten Al-Mg alloy spreads over an iron surface, i.e., the system becomes wettable by alloying magnesium on the present experimental condition. Since magnesium itself does not dissolve in iron or form any intermetallics with iron, the major roles of magnesium to decrease the contact angle are considered to be as follows:

(1) The adsorption of evaporated active magnesium atoms on the iron surface. The adsorption of vapor magnesium atoms on the iron surface would affect the surface free energy (σ_{sv}) and, if σ_{sv} increases, the contact angle decreases as a result.

(2) The adsorption of dissolving magnesium atoms at solid/liquid interface. According to the measurement of the surface tension of the molten aluminum,⁸⁾ magnesium decreases the surface tension of molten aluminum.

(3) Prevention of the oxide layer formation.

According to a model proposed by Nogi *et al.*,⁹⁾ the evaporation of magnesium can prevent the formation of the thin oxide layer at the liquid surface if the amount of evaporation is large enough.

Fig. 1. Schematic view of the experimental apparatus for a measurement of the contact angle.

Fig. 2. Effect of a holding time on the contact angle of Al-Mg alloy on the iron substrate as 893 K.

Fig. 3. The concentration of magnesium in molten Al-Mg drop as a function of a holding time.

Figure 3 shows a magnesium content in the Al-Mg alloys as a function of a holding time. A decrease in magnesium content was apparently observed at both temperatures. Nogi's model is used here to estimate whether the evaporation of magnesium occurs vigorous enough to prevent the formation of the oxide layer. This model describes the role of metal vapor as an oxygen getter. The number of evaporated magnesium atoms and the collision number of oxygen molecules to the wall per unit area and unit period were calculated in a following manner. In this measurement, the pressure of the atmosphere was 1.33×10^{-3} Pa.

The total number of the collision of oxygen molecules to the liquid surface per surface area (Z_{wall}) is defined as Eq. (1).

$$Z_{\text{wall}} = \frac{1}{4} \frac{N}{V} \bar{C} \quad \dots\dots\dots(1)$$

where N is a number of oxygen molecules in volume V , and $\bar{C}$ is an average velocity of the molecules that is defined as:

$$\bar{C} = \left(\frac{8RT}{\pi M} \right)^{1/2} \quad \dots\dots\dots(2)$$

where R and M represent the gas constant and the molecular weight, respectively. From these equations, the oxygen collision numbers at 893 K and 773 K are calculated as 4.15×10^{14} and 4.43×10^{14} mol/s·cm², respectively. The average evaporation number of magnesium atoms was calculated by a measured magnesium content change in Al-Mg drop shown in Fig. 3. According to the calculation, the average evaporation numbers at 893 and 773 K are 3.0×10^{19} and 4.0×10^{18} atm/s·cm², respectively. A comparison between the collision number and the evaporation number at each temperature makes it clear that the evaporation number of magnesium is much larger than the collision number of oxygen molecules and, hence, magnesium vapor is concluded to prevent the oxide layer formation in this experimental condition.

Table 1. Vapor pressure of Al, Mg, Cu and Si at several temperatures.

	Vapor pressure (p^0 /Pa)		
	400 K	700 K	1 000 K
Al	1.14×10^{-31}	2.80×10^{-13}	5.08×10^{-6}
Mg	8.41×10^{-9}	1.12	1.59×10^3
Cu	7.33×10^{-33}	5.02×10^{-14}	1.56×10^{-6}
Si	1.07×10^{-46}	1.61×10^{-21}	1.79×10^{-11}

Fig. 4. Effect of the addition of surface active elements on the contact angle ($t=3$ s) of Al-Mg alloy at 773 K. (a) Bi addition, (b) Pb addition and (c) Li addition.

3.1.2. Aluminum-Copper and Aluminum-Silicon Systems

The contact angles of three copper content levels of Al-Cu alloy (20, 30 and 40 mass% Cu) and Al-11 mass%Si alloy drops were measured on the solid iron substrate at 893 K. The initial contact angles of molten Al-Cu alloys and Al-Si alloy were greater than 90°, indicating molten Al-Cu alloy and Al-Si alloy do not wet iron on a given experimental condition. Moreover, the contact angle held constant for each system including Al-Si alloy regardless of the holding time. Taking the low vapor pressure of copper and silicon (shown in Table 1) and activities of these elements in molten aluminum into account, this is caused by a formation of an oxide film at the surface of the molten drop. Since the inside of the chamber was not evacuated highly enough to prevent the oxide layer formation and the metal vapor did not get oxygen effectively, the surface of the melt drop was covered with oxide film and reliable data could not be obtained. These results made it clear that a critical amount of magnesium alloying would be favorable for aluminum-base filler metals.

3.2. Addition of Surface Active Elements

Contact angle data described in above sections were measured at 893 K because Al-20 mass%Cu alloy, for example, do not melt at temperatures below 873 K. In a practical aspect, the operation temperature of welding

should be as low as possible to avoid a plastic deformation of an aluminum part to be joined. The surface tension of molten metal, however, increases with a decrease in temperature, which indicates that the molten metal and the solid surface tend to be less wettable at lower temperatures. In many cases, an addition of the surface active element is effective to decrease the surface tension and to make the system wettable. In this section, Al-35mass%Mg alloy (melting point: 723 K) is used as a base metal and the effect of surface active elements on the contact angle at 773 K is dealt with.

Lang^{8,10)} reported that the surface tension of aluminum decreased by adding only a minute quantity of a surface active element such as lead, bismuth and lithium. The initial contact angle data ($t = 3$ s) of Al-Mg-Bi drop as a function of bismuth content is shown in Fig. 4(a). The initial contact angle decreases with an increase in the bismuth addition, but reaches to a minimum value with 0.05 mass% addition. The same tendency is also seen in Figs. 4(b) and 4(c) for lead-added and lithium-added systems. These measurements prove that only a small amount of addition of bismuth, lead and lithium is effective to improve the wettability but, on the contrary, an excessive addition hinders the good wettability. This increase in the initial contact angle would probably be caused by a layer of surface active elements at the interface which prevents the interaction between iron and aluminum, *i.e.*, the balance between the surface active effect and the impeding interaction effect would be important. Figure 5 shows the average thickness of the reaction layer at the interface for Fe/Al-35mass%Mg- x mass%Bi ($x = 0.05$ and 0.1) systems. It is clearly seen in the figure that the reaction layer of Al-35mass%Mg-0.05mass%Bi system tends to be thicker than that of Al-35mass%Mg-0.1mass%Bi system. This proves that an excess amount of the surface active element segregates at the interface and, therefore, an interaction between iron and molten aluminum is inhibited to some extent. From a point of view of the interfacial phenomena, finding out the optimum content of surface active elements is a noticeable result. Many reserches¹¹⁻¹³⁾

Fig. 5. Effect of a holding time on the thickness of the reaction layer between Al-Mg-Bi alloy and iron formed at 773 K.

have contributed to identify the interfacial phenomena between iron and aluminum. The formation of many phases such as Fe_3Al , Fe_2Al and FeAl , depending on the experimental condition and the chemical composition of the aluminum alloy, have been reported. In this work, the atomic ratio of Al:Fe measured by X-ray micro-analyzer also varies depending on the position. For the most part of the reaction layer, however, it was nearly 75:25 and magnesium was rarely detected.

3.3. The Temperature Dependence of the Surface Active Effect of Bismuth

In this section, the effect of bismuth addition at different temperatures is dealt with to prove the temperature dependence of the effect of bismuth addition. Figure 6 shows the contact angle of Al-35mass%Mg-0.05mass%Bi alloy on the iron substrate at different temperatures. The initial contact angle data of these systems are plotted as a function of temperature in Fig. 7. The initial contact angles of Al-35mass%Mg alloy at 773 and 893 K are also plotted as filled circles

Fig. 6. Contact angle data for Al-35Mg-0.05Bi drops on iron as a function of a holding time at various temperatures.

Fig. 7. Contact angle data for Al-Mg and Al-Mg-Bi drops on iron as a function of temperature.

Fig. 8. Surface tension of the solvent as a function of the solute content and its temperature dependence.¹⁵⁾

in Fig. 7. By comparing the initial contact angle of Al-35 mass%Mg alloy with that of Al-35mass%Mg-0.05 mass%Bi alloy, the bismuth addition is more effective at 773 K than at 893 K. Considering a few data dealing with the temperature dependence of the surface tension of liquid metals containing surface active elements, these experimental results have a similarity.

Yavoiskii¹⁴⁾ measured a temperature dependence of the surface tension of Fe-C alloys, and reported that the surface tension of Fe-0.002mass%C, which is almost like pure iron, decreases with increasing temperature, *i.e.*, temperature coefficient $d\sigma/dt$ is negative as similar to many metals. However, when carbon content exceeds 0.05 mass%, the temperature coefficient becomes positive at temperatures below 1823 K. This suggest that the carbon is more surface active at lower temperatures than at higher temperatures. P. Kozakevitch reviewed temperature dependence of surface tension as shown in Fig. 8.¹⁵⁾ According to his review, surface-active agents reduces the surface tension of solution more effectively at lower temperatures. P. Kozakevitch also introduces a few results on the temperature dependence of the surface active effect from both calculated and practical data of Pokrovski.¹⁶⁾

3.4. Wettability of Al-Cu-Mg System

Al-Mg alloy has high corrosion resistance and workability but tends to form cavities during solidification in the case of high magnesium concentration. This prevents the usage of Al-Mg alloy of high magnesium content and, therefore, magnesium content should be as low as possible. In order to reduce the content of magnesium, copper was used to decrease the melting point of aluminum alloy and only 1 and 3 mass% of magnesium was added to eliminate the oxide layer. Figure 9 showed a contact angle of Al-Cu-Mg drops. As seen in Fig. 9, the initial contact angle of Al-30mass%Cu alloy was 132°. However, by alloying 1 and 3 mass% of magnesium, the contact angle decreased to 115 and 88°, respectively. Furthermore, 0.05 mass% of bismuth addition was proved to be effective to improve the wettability with iron as already shown in 3.2. Hence, 0.05 mass% bismuth was also added to Al-30mass%Cu-

Fig. 9. Contact angle data for Al-Cu and Al-Cu-Mg drops on iron as a function of time at 893 K.

Fig. 10. Effect of bismuth addition on the contact angle ($t=3$ s) at 833, 863 and 893 K.

3mass%Mg alloy to improve the wettability and the temperature dependence of bismuth's effect was also measured. The result is shown in Fig. 10. As is shown in Fig. 10, the addition of bismuth is more effective at lower temperatures and a contact angle of Al-30mass%Cu-3mass%Mg-0.05mass%Bi alloy drop on iron substrate is less than 90° even at 833 K. Thus, an effectiveness of surface active elements at lower temperatures was proved again in this case.

4. Conclusions

Measurements of the contact angle of molten aluminum alloys (Al-Mg, Al-Si and Al-Cu alloys) on the iron substrate were carried out for the purpose of developing a filler sheet for welding between aluminum and iron. Attempt was also made to improve the wettability by alloying a minute quantity of surface active elements (lead, bismuth and lithium) to aluminum alloy. The contact angle was measured at 773 and 893 K in a vacuum (1.33×10^{-3} Pa) and the results obtained are

summarized as follows:

(1) The contact angle of molten Al-Mg alloy decreases with increasing magnesium addition from 15 to 35 mass%. An evaporation number of magnesium atoms from a surface of molten drop is much larger than a calculated collision number of oxygen molecules to the surface.

(2) Since a thin oxide layer forms at the surface of the molten Al-Si and Al-Cu drops on this experimental condition, accurate contact angle data of these alloys could not be obtained.

(3) Only a 0.05 mass% addition of surface active elements reduces the contact angle of molten Al-35 mass%Mg alloy most effectively. An excessive addition of the surface active elements, however, increases the contact angle.

(4) Compared with Fe/Al-35mass%Mg-0.1mass%Bi system, Fe/Al-35mass%Mg-0.05mass%Bi system tend to form a thinner reaction layer at the interface ($T=773\text{ K}$).

(5) Bismuth is more surface active in molten Al-30mass%Cu-3mass%Mg alloy at 773 K than at 893 K.

Acknowledgment

Partial support for this work was provided by Daido Steel Co., Ltd.

REFERENCES

- 1) O. Ohashi and K. Sasabe: *Weld. Int.*, **4** (1990), 775.
- 2) G. Garmong, N. E. Paton and A. S. Argon: *Metall. Trans.*, **6A** (1975), 1269.
- 3) A. Hill and E. R. Wallach: *Acta Metall.*, **37** (1989), 2425.
- 4) P. M. Bartle: *Weld. J.*, **54** (1975), 799.
- 5) W. A. Owczarski and D. F. Paulonis: *Weld. J.*, **60** (1981), 22.
- 6) T. Takemoto and I. Okamoto: *J. Mater. Sci.*, **23** (1988), 1301.
- 7) T. Enjo: *J. Jpn. Inst. Light Met.*, **39** (1989), 58.
- 8) G. Lang: *Aluminum*, **50** (1974), 231.
- 9) K. Nogi, K. Ogino, A. Maclean and W. A. Miller: *Metall. Trans.*, **17B** (1986), 163.
- 10) G. Lang: *Aluminum*, **50** (1974), 731.
- 11) J. C. Rawers and H. E. Maupin: *J. Mater. Sci. Let.*, **12** (1993), 637.
- 12) S. Ohya: *Met. Technol.*, **59** (1989), 7.
- 13) T. Momono and T. Enjo: *J. Jpn. Inst. Light Met.*, **35** (1985), 396.
- 14) V. I. Yavoiskii: *Surface Phenomena in Metallurgical Process*, ed. by A. I. Belyazev, Consultant Bureau, New York, (1967), 230.
- 15) P. Kozakevitch: *Surface Phenomena of Metals*, Soc. Chem. Industry, London, (1968), 223.
- 16) N. L. Pokrovski: *Ukr. Fiz. Zh.*, **7** (1962), 845.