



Title	Effect of Bismuth Addition to Brazing Sheet Claddings on Fluxless Brazability of Aluminum(Welding Physics, Process & Instrument)
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Citation	Transactions of JWRI. 1983, 12(2), p. 193-201
Version Type	VoR
URL	https://doi.org/10.18910/7753
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Effect of Bismuth Addition to Brazing Sheet Claddings on Fluxless Brazability of Aluminum†

Tadashi TAKEMOTO* and Ikuo OKAMOTO**

Abstract

Fluxless brazing was made in a vacuum down to 2×10^{-5} torr at 600°C for 3 min using Al-10%Si-1%Mg filler alloys containing Bi up to 0.4% in the form of brazing sheet claddings. Fluxless brazing was also made in reduced nitrogen gas atmosphere down to 10^{-1} torr and in purified nitrogen gas at 760 torr using Al-10%Si filler alloys containing Bi up to 0.4%. An addition of Bi particularly 0.05 to 0.1% to brazing sheet claddings improves the length of filled clearance and leg length ratio in all the brazing processes. Although the flow factor is unchanged, the fillet form is homogenized by the use of Bi bearing brazing sheets. Bi freely exists in Al-10%Si filler alloys, while it combines with Mg in Al-10%Si-1%Mg filler alloys. The mechanism of improving the brazability by Bi addition in vacuum brazing processes is attributed to that Mg and Bi or Bi vaporize at low temperatures breaking down the surface oxide film on brazing sheets, and Mg and Bi prevent reoxidation of the fresh surface produced during heating by gettering oxygen in the brazing furnace.

KEY WORDS: (Aluminum Alloys) (Vacuum) (Brazing) (Brazability) (Bismuth) (Fluxless Brazing)

1. Introduction

The vacuum brazing process of aluminum had been remarkably advanced by the development of the brazing sheet with Mg bearing Al-Si-Mg claddings. The prominent feature of the process is the so called "getter action" of Mg in brazing sheet claddings. During heating to the brazing temperature, vaporized Mg from the claddings reacts to the moisture and oxygen in a brazing furnace and traps them, this reaction provides the clean vacuum atmosphere and permits the new clean brazing metal to flow and results in good brazability. Despite the merits of the improvement by the use of Mg bearing alloy, some problems have been remained to be solved due to the adhered Mg and Mg oxide which attached to the furnace walls. They adsorb the moisture and oxygen when the furnace is subjected to air atmosphere, and the removal of them in air atmosphere is rather dangerous and expensive. Therefore, Al-Si-Mg clad alloys with low Mg content are preferable. Many investigations have been performed to lower the Mg content in clad alloys without decreasing the brazability. It has been found that the small addition of Bi enables to decrease the Mg content in cladding^{1,2)} and to improve the flowability and the ability of clearance filling even in the low vacuum level brazing condition³⁻⁵⁾. In the other fluxless brazing processes such as purified

nitrogen gas process at atmospheric pressure and carrier gas process, not only Bi but also Ba, Sb and Sr are regarded as the effective elements^{6,7)}, however, the role of Bi in fluxless brazing has not been clarified yet even the process has already been used in commercial brazing processes.

The aim of this article is to investigate the effect of Bi in the brazing sheet claddings on the fluxless brazability, the existing form of Bi and the role of Bi in the fluxless brazing process.

2. Materials and Experimental Procedures

Brazability was evaluated by the fillet formation test of tee type joint with a vertical brazing sheet member and a horizontal base plate member. The brazing sheets of 1.2 mm thickness are consisted of 1 mm thickness A 3003 core material and 0.1 mm thickness clad material (filler alloy) on both sides. The base plate is A 1100 commercial pure aluminum (0.13%Fe, 0.08%Si, 0.03%Cu, 0.02%Mn, balanced Al). The fundamental composition of filler alloys are Al-10Si and Al-10Si-1Mg, and the alloys contained Bi up to 0.4%. Table 1 gives the chemical compositions of the filler alloy claddings on brazing sheets. Prior to brazing, base plate (A 1100) surface was ground by 600

† Received on October 31, 1983

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

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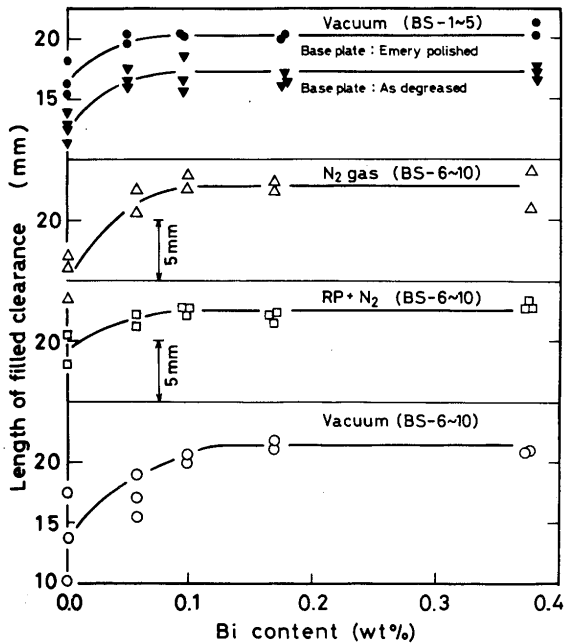


Fig. 3 Effect of Bi content in brazing sheet claddings on length of filled clearance of type A specimen under various brazing conditions.

the other fluxless processes.

The braze results on the length of filled clearance of B type specimen are shown in Fig. 4. In vacuum process (BS-1 ~ 5, base plate surface: as degreased), the length of up side fillet (X_U) was larger than that of down side fillet (X_D) indicating that the alloys had a tendency to gather at lower side. To assure the stable braze results, the longer filled clearance is preferable even the existence of incline in base plate. So the total length of filled clearance, $X_U + X_D$, has the significance to compare the brazability of B type specimen. As well as the A type specimen, the brazing sheets with 0.05 ~ 0.1%B i showed large value of $X_U + X_D$. In purified N_2 process, X_U is longer than X_D in Bi less brazing sheets. The appearance of brazed specimen without Bi showed the surface flow of filler alloy resulting the long horizontal fillet leg length. Due to this surface flow of molten filler alloy on base plate, X_D by purified N_2 process seems to be decreased. Similar to the vacuum brazing process, the addition of 0.05 ~ 0.1%B i gives large $X_U + X_D$.

3.2. L_V/L_H

Figure 5 shows the effect of Bi content on L_V/L_H in various brazing methods. In vacuum process using emery polished base plate, L_V/L_H exceeded the value of 0.95 irrespective of the Bi content in brazing sheet claddings. All fillets exhibited excellent fillet form meaning that Bi addition had no effect on L_V/L_H in the case of emery polished base plate. However, in the case of as degreased

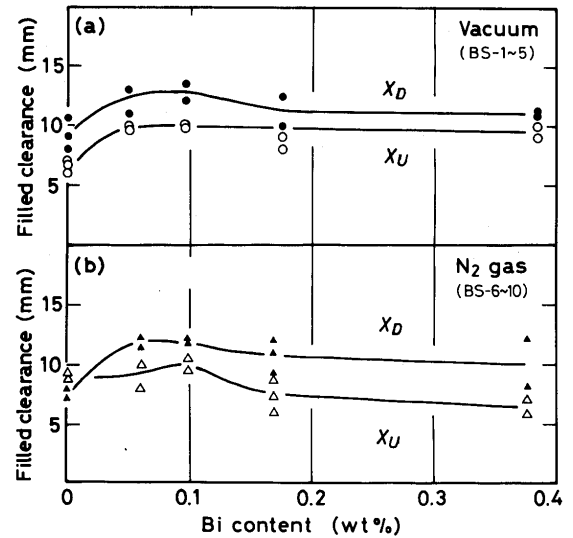


Fig. 4 Effect of Bi content in brazing sheet claddings on length of filled clearance of type B specimen under vacuum and purified nitrogen gas

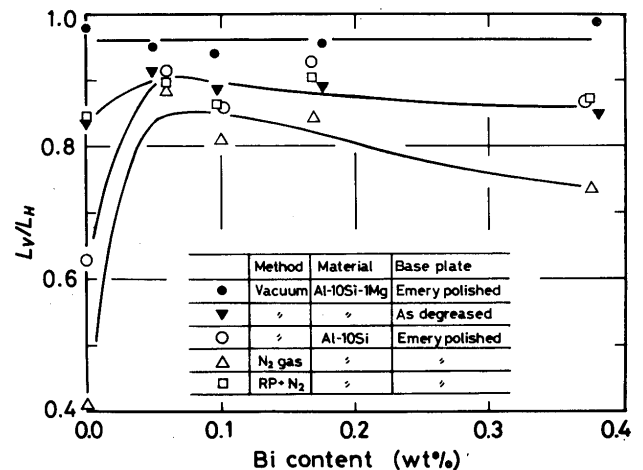


Fig. 5 Effect of Bi content in brazing sheet claddings on L_V/L_H

base plate, the small addition of Bi increased L_V/L_H , the values were slightly smaller than those of emery polished base plate. The effect of small addition of Bi on the rise of the values of L_V/L_H is also evident in the fluxless brazing methods with Mg less BS-6 ~ 10, especially the improvement effect is remarkable in vacuum and purified N_2 gas processes. In vacuum and purified N_2 gas processes with Mg less brazing sheets, the molten filler alloy flows on the horizontal base plate, which provides bad fillet form with long L_H , resulting low values of L_V/L_H ranging 0.4 ~ 0.6. However, the addition of 0.05%B i improved the brazability remarkably and the values exceeded 0.85. The addition of Bi exceeding 0.1% seems to have no further favourable effect on L_V/L_H . The results of L_V/L_H indicates that the addition of 0.05 ~ 0.1%B i is sufficient for the improvement of brazability. In addition to this, similar to the

length of filled clearance, the effect of Bi addition is the most dominant in purified N₂ gas process.

Figure 6 shows the flow factor of each brazing sheet in various brazing processes. In vacuum and carrier gas processes, the values are almost constant (about 0.6) irrespective of Bi content. In purified N₂ process, the flow factors of Bi bearing brazing sheets seems about 10% larger than those of Bi less brazing sheets. The exact reason is not known, however, the length of filled clearance in Bi bearing alloys are about more than 40% longer than Bi less alloys. The extended filled clearance seems to depend not only on the difference in flow factors but also the other factors such as the spread loss. A part of the molten filler alloy flew on the base plate which gave any contribution to the fillet formation. The case of low L_V/L_H value with large L_H should result in the large crosssectional fillet area. Therefore under the condition of the same volume of molten filler alloys, the length of filled clearance becomes short.

The appearance of the fillet of A type specimen is slightly different in BS-1 ~ 5 as shown in Fig. 7. The fillet size distribution along longitudinal direction is not uniform in Bi less BS-1 (Fig. 7(a)), however, the distribution is uniform in Bi bearing alloys as shown in Fig. 7(b) and (c). It is clear that the uniform distribution of fillet offered the long filled clearance. The ununiformity of the fillet size distribution is pronounced in the filled clearance test specimen (A type). In the usual inverse tee type specimen, fillet size distribution was rather uniform even in Bi less specimen as shown in Fig. 8.

Under the hypothesis that the length of filled clearance is represented by the similar equation to the capillary

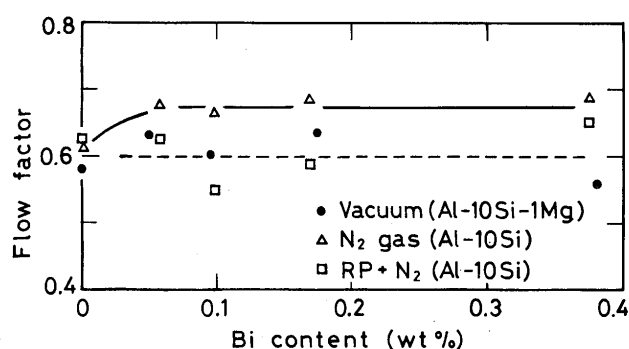


Fig. 6 Effect of Bi content on flow factor of brazing sheet

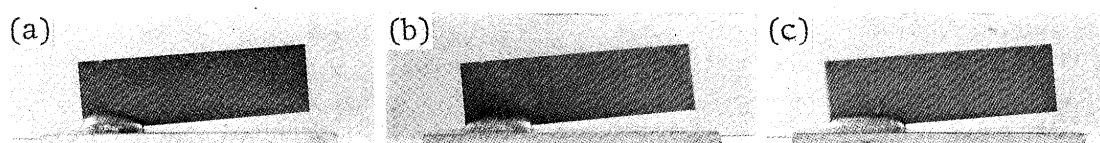


Fig. 7 Appearance of brazed specimens of type A, (a) BS-1, (b) BS-3, (c) BS-4

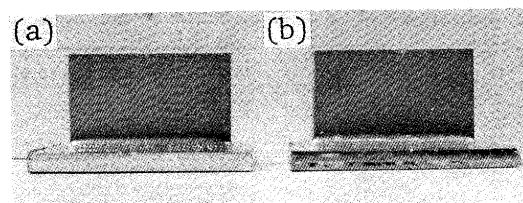


Fig. 8 Appearance of brazed tee type specimens, (a) BS-1, (b) BS-4

length between the two vertical parallel plates⁹⁾, the length of filled clearance will follow the following equation.

$$X_H = k (\gamma_s - \gamma_{\ell s})$$

X_H : length of filled clearance

γ_s : surface tension of solid

$\gamma_{\ell s}$: interfacial tension between solid and liquid

k : constant depends on density, gravity, clearance and etc.

From Young-Dupre's equation, $\gamma_s = \gamma_{\ell} \cos \theta + \gamma_{\ell s}$, Eq. (1) is represented as follows;

$$X_H = k \cdot \gamma_{\ell} \cos \theta$$

γ_{ℓ} : surface tension of liquid

θ : contact angle

As γ_{ℓ} is considered to decrease by the addition of Bi to brazing sheet claddings^{1), 10), 11)}, increment of X_H by addition of Bi is seemed to be attributable to the decrease in θ which means that the addition of Bi promoted wetting.

3.3. Scanning electron microscopic observations

The surface of brazing sheet of as received condition and after brazing heat cycles was observed by scanning electron microscope. Secondary electron images of the as received surface of BS-5 and 10 are represented in Fig. 9, where the line analysis of each element is also shown. The analyzed position is the horizontal white line at center of micrographs. For examples of Bi bearing alloys with and without Mg, the results of BS-5 and 10 are shown in Fig. 9. In Mg bearing BS-5, Bi exists together with Mg. On the other hand, in Mg less alloys, Bi freely exists, which

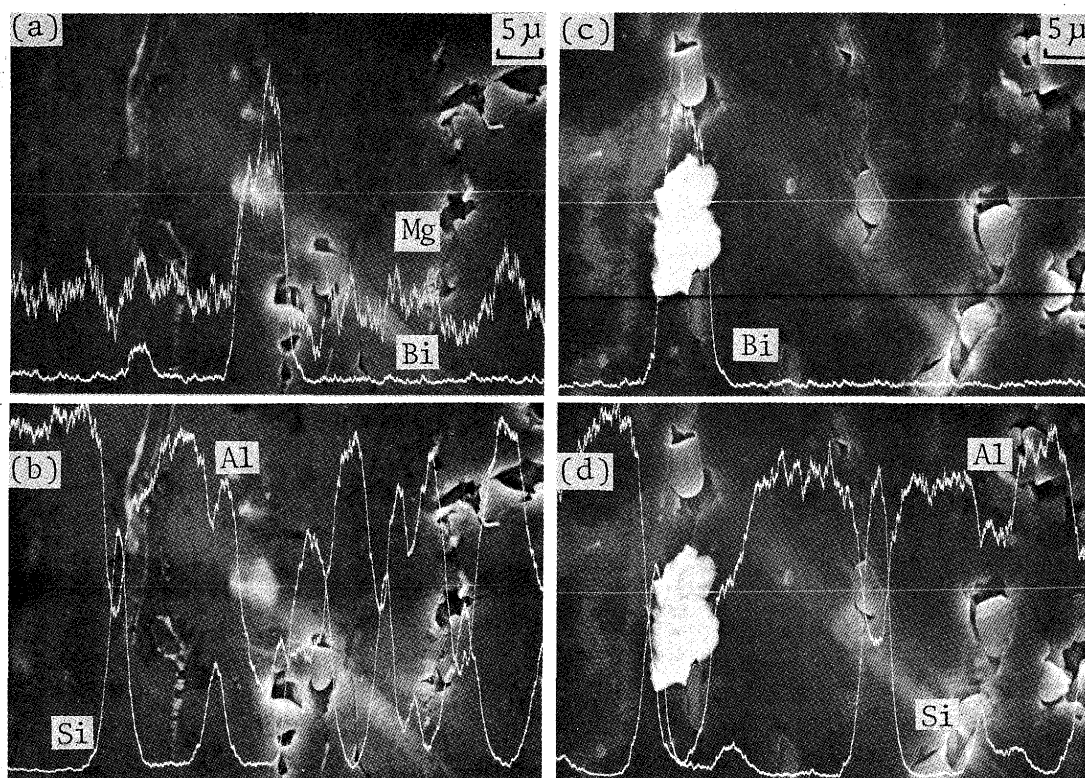


Fig. 9 Scanning electron micrographs and energy dispersive line analysis of brazing sheets of as received, (a) (b) BS-5 (Al-10Si-1Mg-0.4Bi), (c) (d) BS-10 (Al-10Si-0.4Bi)

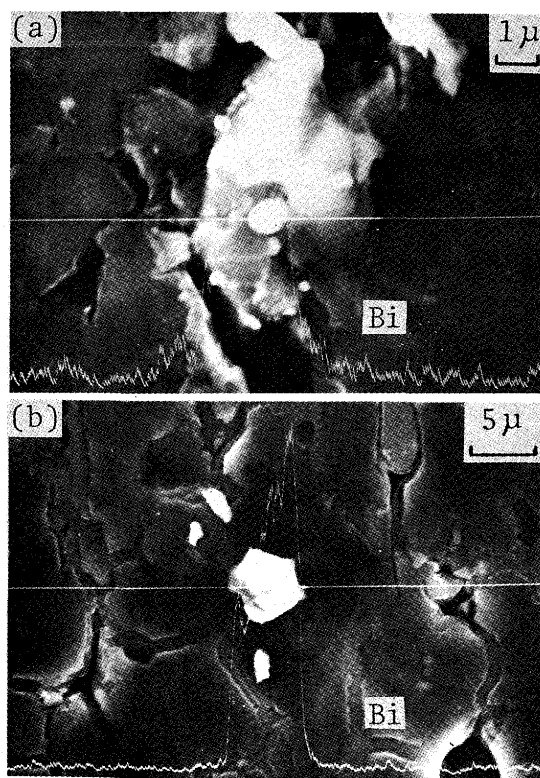


Fig. 10 Scanning electron micrographs and energy dispersive line analysis of brazing sheets after heating at 520°C for 20 min in vacuum, (a) BS-5, (b) BS-10

corresponds that Bi does not dissolve into Al and Si¹²⁾. Figure 10 is the micrographs of BS-5 and 10 after heating at 520°C for 20 min in a vacuum. In Mg bearing alloys, a part of particles containing Bi becomes somewhat globular and the surrounding part exhibits the figure like a crater. Due to the existence of Al-Mg-Bi system ternary eutectic point at 435°C¹³⁾, the Bi rich portion has once melted when heated to 520°C and a part of Bi and Mg has vaporized. On the contrary, Bi freely existed in Mg less BS-10 brazing sheet. Bi particle begins to melt at its melting point, 271°C, so the every Bi particle showed relatively globular shape. As the Bi particle in BS-10 is larger than the Bi containing particle in BS-5, the vaporization rate of Bi is slower in the former brazing sheet.

Figure 11 shows the surface of brazing sheet after heating at 555°C for 20 min in a vacuum. The differential thermal analysis on filler alloy with the same composition as BS-5 cladding revealed that the alloy has already partially melted at this temperature. As shown in the micrographs, it was difficult to find out the particles containing Bi in BS-5 and 10, therefore almost of Bi in brazing sheet claddings were supposed to be vaporized. On the other hand, in purified N₂ gas, the Bi containing particles were presented in both BS-5 and 10 after heating at 555°C for 20 min (Fig. 12), indicating that the vaporization rate of Bi in purified N₂ atmosphere at 760 torr

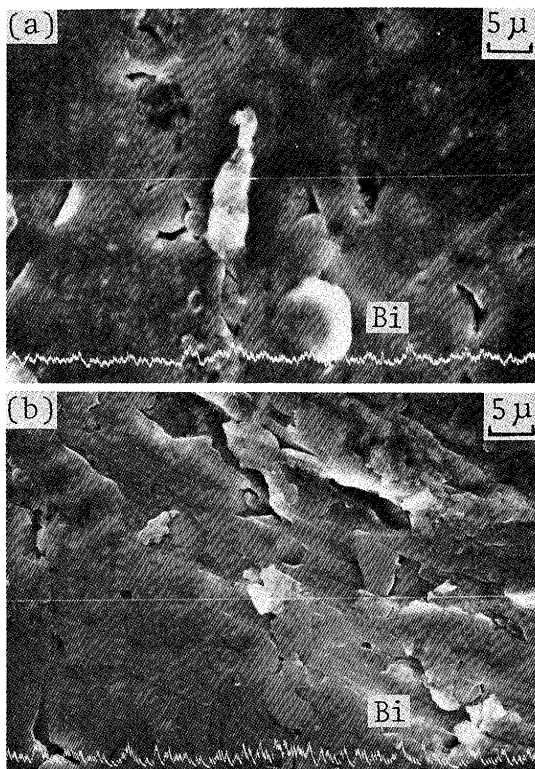


Fig. 11 Scanning electron micrographs and energy dispersive line analysis of brazing sheets after heating at 555°C for 20 min in vacuum, (a) BS-5, (b) BS-10

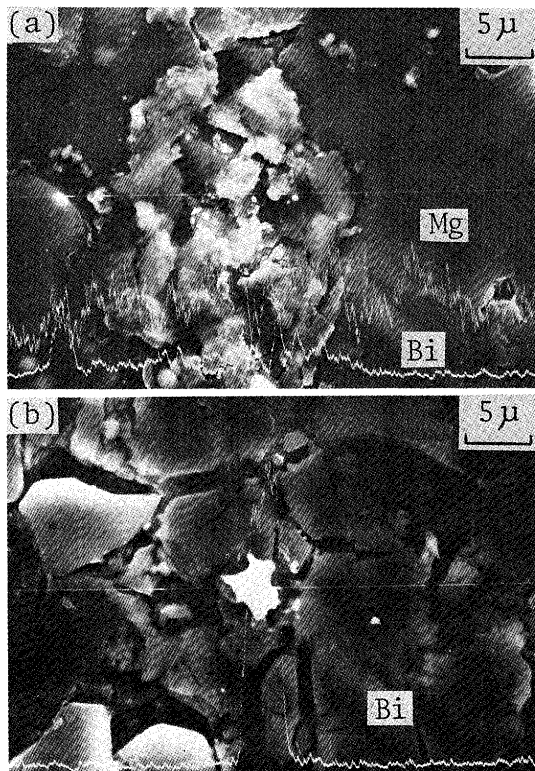


Fig. 12 Scanning electron micrographs and energy dispersive line analysis of brazing sheets after heating at 555°C for 20 min in N₂ gas (a) BS-5, (b) BS-10

was slower than in a vacuum of 10^{-5} torr.

It was difficult to find out the Bi containing particles by energy dispersive analysis on brazing sheet surface after brazing. The electron probe analysis by Kawase *et al.*¹⁾ found similar results, so the Bi seems to have been completely vaporized during brazing heat cycle. Figure 13 shows the Auger spectrum by Auger electron spectroscopy on BS-3 after vacuum brazing. The clear peaks of O₂, MgO, Al₂O₃, Si and also the small peaks of Bi and Ca appear. After Ar sputtering for 1 min (2 kV, 30 mA), the peaks of Bi, Ca and MgO become small and the spectrum of Al₂O₃ changes. As the spectrum of Bi also changes, it seems that the Bi existed as oxide at surface layer. By further sputtering, the spectrum of Al₂O₃ changes into Al and after 4 min sputtering, the spectrum completely becomes to the spectrum of Al. Fig. 14 shows the relations between the peak to peak height of oxygen and the sputtering time. As mentioned above, after sputtering for 4 min, the spectrum of Al₂O₃ changed into Al in BS-3, but in Mg less BS-8 it took about 40 min to change the spectrum of Al₂O₃ to Al completely indicating that the surface oxide film is thicker than that of Mg bearing alloys. The Auger peak to peak height of Bi drastically decreased by short time sputtering, which means that the Bi existed extremely at the surface. The decreasing rate of the height of Bi in BS-3 after vacuum brazing was higher than in BS-8 after carrier gas and purified N₂ gas brazing showing that the vaporization amount was large in the vacuum brazing method.

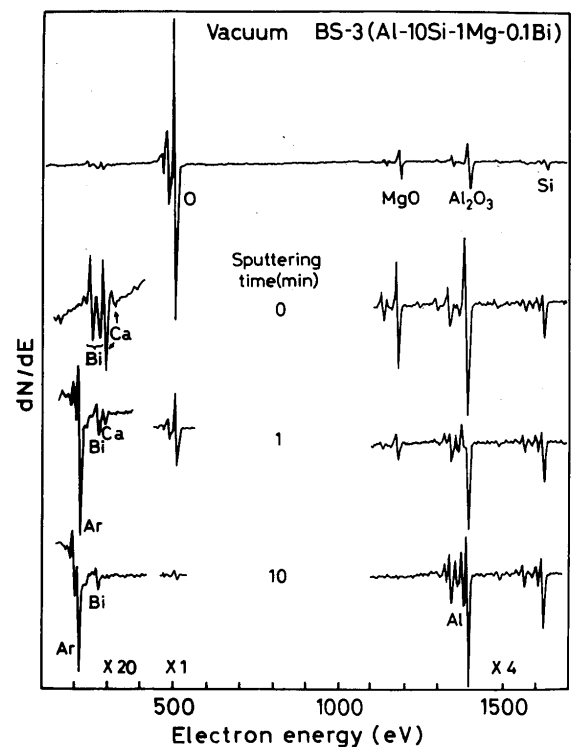


Fig. 13 AES of BS-3 after vacuum brazing

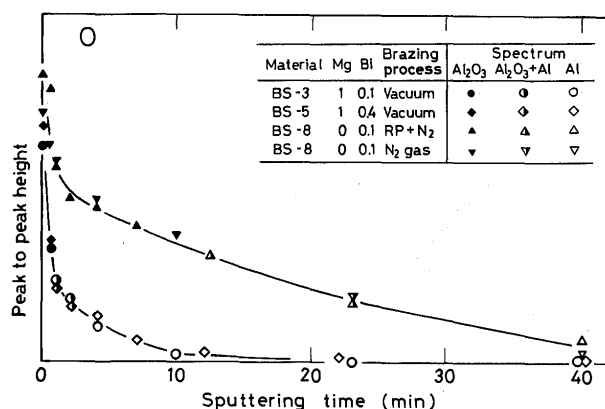


Fig. 14 Effect of sputtering time on the changes of Auger peak to peak height of oxygen of brazing sheets after brazing, the different marks corresponds the kinds of spectrum of Al₂O₃ and Al

4. Discussions

It is found that the addition of 0.05 ~ 0.1%B_i to brazing sheet claddings is preferable for the improvement of fluxless brazability of aluminum. The improvement by Bi addition is more clear under the brazing processes in a vacuum and in purified N₂ gas at atmospheric pressure of 760 torr. The amount of water vapor of N₂ gas with the dew point of -68°C corresponds to the vacuum level of less than 10⁻³ torr. On the other hand, in N₂ carrier gas, the impurity level is estimated by the product of the purity of N₂ gas (exceeds 99.99%) and the vacuum level (more than 10⁻¹ torr), i.e., 10⁻⁴ × 10⁻¹ = 10⁻⁵ (torr)¹⁴. Therefore, the impurity level of N₂ carrier gas atmosphere is estimated less than 10⁻⁵ torr, and the purity level of brazing atmosphere decreases in this order: N₂ carrier gas process, vacuum process, purified N₂ gas process at 760 torr. The braze results of Bi less BS-6 showed that L_V/L_H became low according to the above mentioned order. But the addition of 0.05%B_i remarkably increased L_V/L_H and gave almost the same value of L_V/L_H irrespective to the brazing conditions. The remarkable improve effect of Bi addition exerts only under the condition that the atmosphere of brazing system is relatively not so good. This corresponds well with the braze results that the additional effect of Bi in vacuum brazing process exerted remarkably under low vacuum level^{3),4)}.

The following discussion deals with the effect of Bi addition to the Mg bearing filler alloys on the brazability. Generally, one of the roles of Mg in Al-Si filler alloy is considered to be the gettering action of Mg against the oxygen and moisture in brazing furnace and the breakdown effect of surface oxide film by the sublimation and vaporization of Mg. In addition to this, thermodynamical calculation by Terill *et al.*¹⁵⁾ indicated that Mg can reduce

Al₂O₃. On the other hand, Bi can react only with O₂. Therefore, so called getter action of Mg is considered to be considerably stronger than that of Bi. Winterbottom *et al.*¹⁶⁾ measured the sublimation and vaporization rate of Mg in brazing sheet claddings during heating in a vacuum. The results showed that the Mg vaporization rate suddenly increased at the Al-Si-Mg ternary eutectic point (551°C*). Anderson¹⁷⁾ pointed out that the cracks due to the Mg sublimation and thermal grooving became remarkable at 550°C and the partial melting occurred at 560°C, that is just above the ternary eutectic point. From their observations, it is considered that vaporization of Mg became vigorous after melting of filler alloys. As indicated in Fig. 9, Bi existed with Mg in Bi bearing alloys, if the elements formed Al-Mg-Bi ternary eutectics, the filler alloy began to melt at 435°C¹³⁾. The getter action of Bi bearing filler alloys is supposed to become active at relatively lower temperature than Bi less alloys, therefore, the effect of Bi addition becomes more effective under the condition that the furnace circumstance is relatively bad.

The effect of Bi addition to Al-Si filler alloys without Mg has been interpreted by the lowering effect of surface tension of filler alloys⁷⁾. The following discussions deal with the improvement mechanism in vacuum brazing process using Mg less filler alloys. As there is no gettering action by Mg in fluxless brazing process using Mg less filler alloys, the reduction of surface oxide on aluminum is essentially impossible. Therefore, the appearance of fresh clean aluminum surface by the breakdown of surface oxide due to the difference in thermal expansion coefficient between oxide and bulk aluminum is the necessary condition to provide the good wetting between the base plate and molten filler alloy¹⁸⁾. If the residual adsorbed components in the brazing furnace react with the fresh clean surface produced by the thermal expansion difference, the fresh surface formed oxide films and the brazability will be reduced.

Figure 15 shows the changes of the vacuum level during vacuum brazing. The vacuum level at the beginning of heating is about 2 × 10⁻⁵ torr. The condition A corresponds the vacuum level change of the brazing furnace that has been maintained open to air atmosphere for a day. Since the amount of adsorption of moisture and gas in air atmosphere is relatively high, the vacuum level becomes very bad during heating to brazing temperature.

* The temperature is slightly different in some articles (for example, H. Watanabe, E. Sato: J. Japan Inst. Light Metals, 19 (1969), 449), however, Winterbottom *et al.* noted that the temperature was 551°C. The differential thermal analysis on filler alloys with the same composition of BS-1 cladding obtained the solidus temperature of 551°C.

Table 2 Effect of bismuth addition to brazing sheet claddings on brazability under relatively bad vacuum level A shown in Fig. 7. Condition B represents the results obtained under good vacuum level.

Brazability	Vacuum condition	BS-6 (0.0Bi)	BS-7 (0.057Bi)	BS-9 (0.167Bi)	BS-10 (0.374Bi)
L_V/L_H	A	0.3	0.89	0.87	0.86
	B	0.63	0.91	0.95	0.87
Length of filled clearance(mm)	A	8.3	15.9	20.9	21.0
	B	13.7	17.1	21.5	20.8

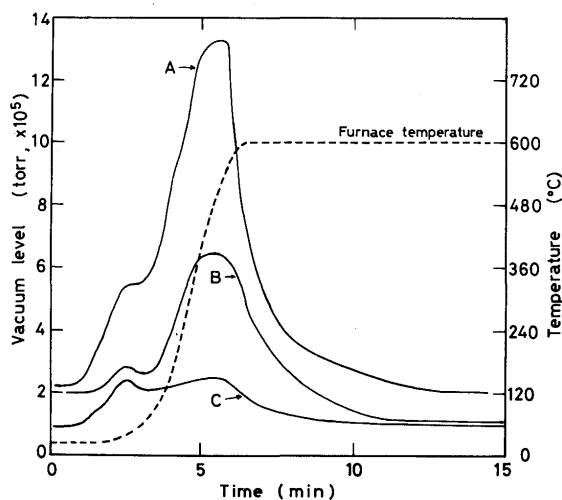


Fig. 15 Changes of vacuum level during brazing heat cycles

The condition B is the normal vacuum level change during brazing (corresponding to the vacuum brazing condition shown in Fig. 3 and 4), and C is the change of the vacuum level of the furnace that reheated without opening to the air atmosphere. In order to investigate the effect of Bi addition to Al-Si filler alloys under the low vacuum level condition, vacuum brazing was carried out under the condition A. The results are shown in **Table 2**. For comparison, the results under the condition B already shown in Fig. 3 and 5 are also indicated. In the case of Bi less BS-6 (Al-10Si), it is clear that L_V/L_H and the length of filled clearance are lower under the condition A than condition B. However, in Bi bearing alloys there is no difference between condition A and B. The results are similar to the effect of Bi addition to the Al-Si-Mg system filler alloys that the improvement by Bi addition is more dominant in low vacuum level condition. The vacuum level reached the lowest value after heating for 6 min, where the furnace temperature exceeded 500°C and the surface temperature of base plate and brazing sheet were also expected to be relatively high. The low value of L_V/L_H and the length of filled clearance in Bi less BS-6 might be attributed to the reoxidation of base material

and brazing sheet. Therefore, during heating stage to brazing temperature, the prevention of reoxidation of oxide free matrix, produced by the thermal expansion difference between oxide film and matrix metal, seems to be very important. Added Bi to Al-Si filler alloys melted at 271°C and it seemed to remain until the beginning of flow of filler metal. Bi can trap the oxygen in the brazing furnace by the oxidation of itself¹⁵⁾. And moreover, as the vaporization temperature of Bi at 10^{-5} torr is about 400°C¹⁾, the preferential oxidation of vaporized Bi traps the oxygen in furnace and suppresses the reoxidation of fresh clean aluminum surface produced by thermal stress. The experiments by Terill *et al.*¹⁵⁾ showed that the Bi set in brazing furnace as a getter material had no improvement effect on brazability. Their experiments also pointed out that Sb also had no improvement effect, however, the addition of Sb in Al-10Si-0.4 ~ 0.7Mg brazing sheet claddings improved the flow factor and brazability¹⁾. Thus Bi and Sb exerted the improvement effect only by the addition to filler metals. It seemed to be effective that the breakdown of the surface oxide film on filler alloy by the vaporization of the elements with high vapor pressure¹⁾ and the ability of gettering action for oxygen¹⁵⁾.

5. Conclusions

The effect of Bi addition to brazing sheet claddings have been investigated using fluxless brazing methods such as vacuum, purified N₂ gas at 760 torr and N₂ carrier gas at 10^{-1} torr. The clarified results are summarized as follows;

- (1) The Bi addition to Al-10%Si and Al-10%Si-1%Mg claddings is effective to the improvement of brazability such as the length of filled clearance and L_V/L_H in fluxless brazing methods. The additional amount of 0.05 ~ 0.1%Bi is preferable irrespective of Mg content in filler alloy claddings and brazing methods.
- (2) The difference in flow factor due to the Bi addition is almost negligible, therefore, the improvement of the length of filled clearance is attributed to the uniform-

ity of fillet form along the longitudinal direction.

- (3) Added Bi to brazing sheet claddings freely exists in Al-Si filler alloys and it combines with Mg in Al-Si-Mg alloys.
- (4) The Bi and the Bi containing particles in filler alloys are almost completely vaporized during heating at 555°C for 20 min in a vacuum and the extremely small amount of residues remains at only thin surface region. On the other hand, in N₂ gas at 760 torr, the Bi containing particles are still remained after heating at 555°C for 20 min.
- (5) The improvement mechanism by the addition of Bi to brazing sheet claddings is believed as follows. In Bi bearing filler alloys, Mg and Bi or Bi vaporize at relatively low temperature and this action breaks down the surface oxide films on brazing sheet surface and Bi reacts with the oxygen in furnace and prevents the oxidation of the fresh surface beneath the surface oxide cracks which formed during heating of brazing and thus provides the excellent brazability.

Acknowledgement

The authors would like to appreciate to Prof. Toshio Enjo and Dr. Toshio Kuroda for the kind assistance on the Auger electron spectroscopy. Thanks are also to the members of the committee of low temperature joining at Japan Light Metal Welding and Construction Society for preparation of brazing sheets and helpful discussions.

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