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A Study on Tunneling Flow of Filler Metal in Aluminum Brazing†

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Abstract

In spreading test of filler metal A1-12%Si alloy (BA4047) on an aluminum plate (1100), the flow (tunneling flow) of molten filler metal sometimes occurs under oxide film formed on the base plate. The purpose of this work was to find various conditions, in which the tunneling flow can be occurred. Experimental results showed that the process of oxide film formation on the base metal and the ratio of spread area to oxide removed area in tunneling flow are important. Moreover, the tunneling phenomena can be applied to the evaluation of the oxide film removability of fluxes.

KEY WORDS: (Aluminum) (Brazing) (Oxides) (Fluxes) (Interfaces)

1. Introduction

On the surface of aluminum, there is a film of aluminum oxide, which can not be wetted by filler metal in ordinary brazing processes. Usually, fluxes as other methods must be employed to remove this refractory oxide film in the brazing of aluminum or in the spreading test of filler metal on aluminum specimen¹)~4).

Even though liquid filler metal can not spread on aluminum oxide surface, sometimes, a good under oxide film flow of filler metal can be found in brazing or spread testing of aluminum. This special phenomena can be called "tunneling flow", which more or less had been mentioned by some authors⁴)5). But the precise character and behavior of tunneling flow remain dark up to now.

On the one hand, the tunneling flow is one kind of defects in aluminum brazing and on the other hand it has some character of flow between metal and oxide. So that the study of the behavior of these phenomena is rather interesting.

In present investigation attention has been confined to some experiments about various conditions, with which the tunneling flow can be occurred, about the character of tunneling flow and the application of these phenomena.

2. Experimental procedure

Figure 1 shows the schematic apparatus for the usual spread tests (without and with flux) used in this experi-

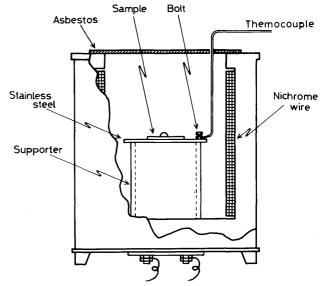


Fig. 1 Schematic apparatus for spread test

ment. Al 1100 plate (thickness of 2mm) was used as base metal and Al-12%Si alloy wire (BA4047, dia, 1.6mm) was used as filler metal. Several kinds of oxide film on Al 1100 base metal were tested, that is; as received state, by oxidizing in air atmosphere and by treating in boiling deionized water. Fluxes used are mainly mixtures of 54%KCl-30%NaCl-16%LiCl chloride and 54.2%AlF₃-45.8%KF fluoride. Spread area was measured by a planimeter.

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3. Results and Discussions

3.1 Tunneling phenomena with and without flux in air atmosphere

At first, we tested the tunneling process by pinpricking that is; the base metal (Al 1100) of as received state and filler metal were heated in the furnace (as shown in Fig. 1) to 620°C, and a pin is used to break oxide films of filler metal and base metal only in small pin area. After that melted filler metal erodes the specimen and flows under oxide film (tunneling phenomena). The flow continues several minutes. In this period the area of tunneling increases with the time. Secondly, as shown in Fig. 2, filler metal (82mg) is put on the position A and chloride

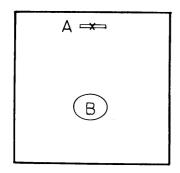


Fig. 2 Spread test with pinprick and with flux

only flux (70mg, 54%KCl-30%NaCl-16%LiCl) is put on the position B. After heating, the pinprick test at the position A is made. After pinpricking, tunneling flow occurs also at the position B. But, if the fluoride contained flux (70mg, 15% fluoride - 85% chloride) is put on the position B, after pinpricking at the position A the tunneling flow can not pass through the position B.

The third test is done by using fluxes (15% or 6% fluoride - 85% or 94% chloride) without the pinprick. A constant weight (82mg) of the filler metal together with various amounts of the flux is placed at the center of the specimen. After heating, the apparent spread area is measured and the results are shown in Fig. 3.

The apparent spread area varied with the flux amount. When the flux amount is less than 80mg in the case of 15% fluoride-85% chloride flux, the apparent spread area is larger than ordinary spread area, because in this region the apparent area consists of tunneling flow area and some part of ordinary spread area. When the flux amount is more than 80mg, the apparent area is only ordinary spread area. This phenomenon is also seen by 6% fluoride -94% chloride flux in Fig. 3. But the transition point is different. In this case, when the flux amount is less than 30mg, there is tunneling flow and apparent area is much more than ordinary spread area. If the flux amount is

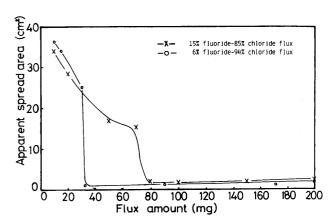


Fig. 3 Relationship between apparent spread area and flux

large enough and the weight of filler metal is constant, the spread area is almost constant. This area is ordinary spread area as we called it.

Afterwards, several serious photographs were taken to record the tunneling process including the pinprick tunneling and the tunneling with flux. The typical appearances of tunneling in various times are shown in Fig. 4 (a) and (b).

Tunneling area and the average of increasing area with respect of time are shown in Fig. 5 and Fig. 6. The surface and cross section of tunneling are shown in Fig. 7 and Fig. 8. Comparing the Fig. 4 (a) with Fig. 4 (b), and Fig. 5 with Fig. 6, we believe the tunneling phenomena with flux and without flux almost have same character and behavior. The difference is the mechanical destruction of the oxide film by the punprick and the chemical removal of oxide film in small size in the case of using small amount of flux. In both cases, after tunneling for several minutes, tunneling rate slowed down and graduately stopped. By using SEM analysis, the change of Si content is detected. Si content is gradually decreased from starting point of tunneling to the end of the tunneling. So that the stop of the tunneling may be explained by change of composition and fluidity of molten filler metal in the process of the tunneling. In Fig. 7 and Fig. 8, we find blow holes in the cross section and on the surface of the tunneling. This was caused by gas evaporation in the process of tunneling. Moreover, at the starting point of pinprick (A position), erosion of the base metal by liquid filler metal was seen before the tunneling phenomena.

From these results, the tunneling phenomena occur only when a small part of oxide films of base metal and filler metal is broken mechanically by pinpricking or removed chemically by using a small amount of fluoride flux. In the process of tunneling, some gases evaporated making blow holes on the surface of tunneling. Existence of oxide film is necessary for continuation of tunneling phenomena.

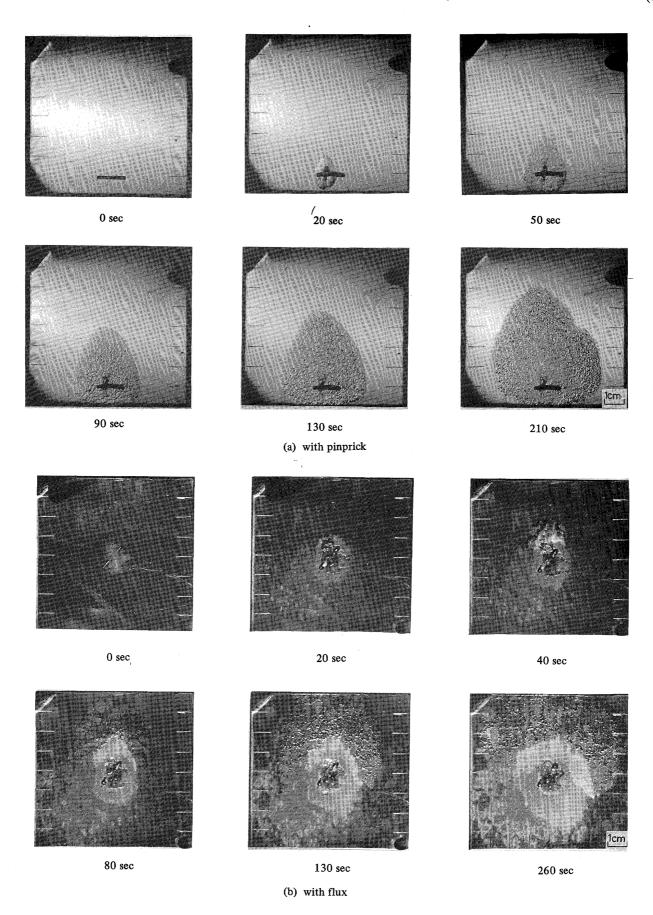


Fig. 4 Changes of appearance of tunneling with holding time

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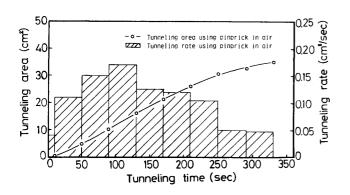


Fig. 5 Relationship between tunneling area and holding time, tunneling rate and holding time with pinprick

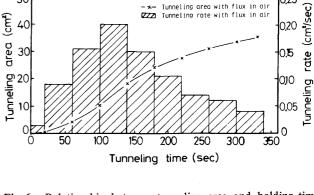
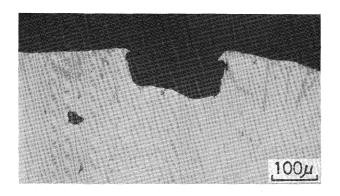


Fig. 6 Relationship between tunneling area and holding time, tunneling rate and holding time with flux



(a) blow hole part

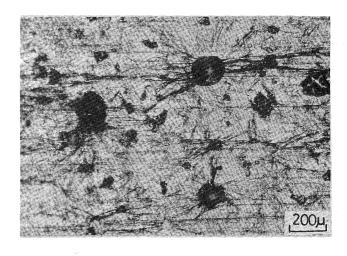
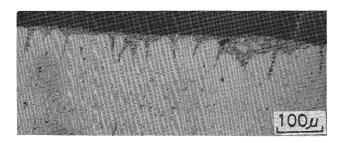


Fig. 8 Surface of tunneling specimen



(b) front part of tunneling

Fig. 7 Cross section of tunneling specimen with pinprick

3.2 Evaluation of oxide film removability of fluxes

As described in the above section, in the pinprick tests using fluoride flux on the position B in Fig. 2, the tunneling flow could not pass through the position B. This phenomenon is considered to be able to evaluate the oxide film removability of various fluxes. As shown in Fig. 9, on the specimen filler metals (each weight 40mg) are put on the position A_1 , A_2 , A_3 , A_4 and also flux is put on the center of the specimen. After heating, the pinpricks were done at A_1 , A_2 , A_3 , A_4 positions. After pinprick test, non tunneling area on the position B was measured and the relationship between non tunneling area and flux amount is shown in Fig. 10. One example of the specimens after testing is shown in Fig. 11 in the case of using 15% fluoride contained flux. From Fig. 10, in the

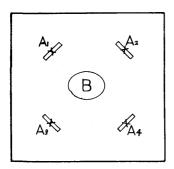


Fig. 9 Test for evaluation of removability of oxide film

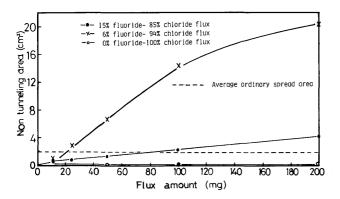


Fig. 10 Relationship between non tunneling area and flux amount

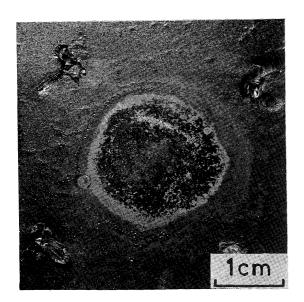


Fig. 11 Specimen after evaluation test; non tunneling on center part.

case of using chloride only flux (without fluoride) tunneling flow passes through the position B covered with molten flux, therefore non tunneling area is about 0cm^2 . However, in the cases of 6% and 15% fluoride contained fluxes, tunneling flow stops at position B. The non tunneling area increases with the increase of flux amount. The area difference of both fluoride fluxes is depended on the melting point and spread-ability of fluxes themselves. The result shows that addition of 6 weight percentage of fluoride to chloride flux in above mentioned compositions is efficient to remove the oxide film. Next, simillar pinprick tests were done with fluxes of different composition (see **Table 1**).

Table 1 Compositions of experimental fluxes

Salt	Weight Percentage						
	No 1	No 2	No 3	No 4	No 5	No 6	
KCl	42	35	51.		50	54	
NaCl.		35	28			26	
LiCl	58	20	15	88	32		
SrCl2		5					
ZnCl2					8	12	
NaF					10		
LiF				12		8	
KF		5					
AlF_3			6				

The results are shown in Fig. 12. No.1 flux has no removability of oxide film, whereas No. 6 flux shows a

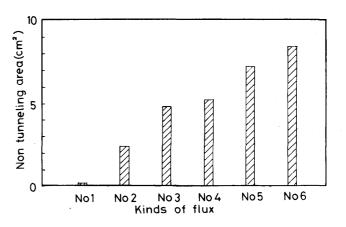


Fig. 12 Removability of oxide film of fluxes with different compositions

good removability for oxide film.

As shown in Fig. 3, the ordinary spread area is about constant in the case of enough amount of flux. This value of spread area is shown in Fig. 10 as a dotted line. As is visible in the figure, this line intersects at about 80mg of flux amount for the curve of 15% fluoride flux and at about 20mg of flux amount for the curve of 6% fluoride flux. These values of flux amount fairly coincide with both values of flux amount that the apparent spread area increases suddenly in Fig. 3. Although this agreement is dependent on the constant amount of filler metal to be used, it is believed from this consideration that when the ratio of spread area to oxide removed area is bigger than unity, tunneling flow took place in spreading test.

3.3 Relation between methods of oxide film formation and tunneling phenomena

In order to get tunneling phenomena, it is necessary to destroy some part of oxide films on the base metal and the filler metal. In the tunneling process, the existing of oxide film on the surface of the base metal and evaporation of gases are important. Because the tunneling phenomena occur at the interface of metal/oxide film, so that different condition of oxide film formation may give a big influence to this kind of phenomena. In order to make sure phenomena, different kind of methods of oxide film formation on the specimens are adopted. For example, by heating specimens in air atmosphere or boiling specimens in deionized water. According to the report of Kawase and et al.6), after heating Al 1100 at 300 to 450°C (1.5hr) in air, the thickness of oxide film is below 100Å. But according to the report of Yamada and et al.⁷), after 5 min boiling in deionized water, the thickness of oxide will be increased to 2000 Å (0.2μ) .

In this work, three groups of specimens are tested. In the first group (No.1) specimens were ground with emery paper (No.1000) and then boiled in deionized water with various periods of time. In the second group (No.2) specimens were chemical etched by 10%NaOH solution and neutrarized by dil. HNO₃ solution and then boiled in deionized water with various periods of time. In the third group (No.3) specimens were chemical etched (same as No.2) and after that oxidized in air at 125°C with various periods of time. After such treatments, all the specimens together with the filler metal (40mg) are heated to 620°C and then pinpricked to test the tunneling ability of these specimens. The holding time after pinpricking at this temperature is 2 min. The relationship of tunneling area and treatment time is shown in Fig. 13. As shown in Fig. 14, according to the behavior and shape after tunneling, the tested specimens are divided into 4 types. In I

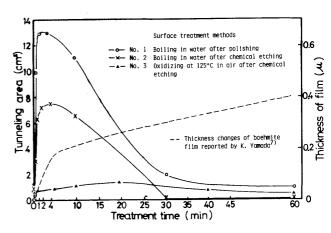


Fig. 13 Relationship between tunneling area and treatment time

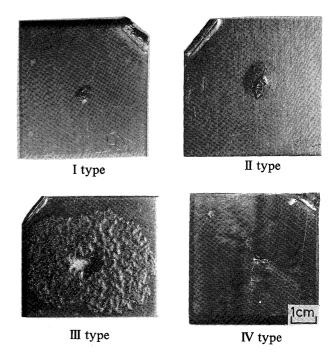
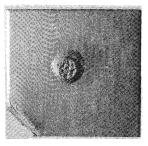
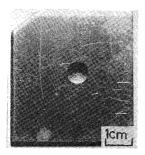


Fig. 14 Classification of tunneling behavior

type, after pinpricking there is no tunneling phenomena and spreading on the specimens. In II type, there occurred severe erosion in the base metal. But there is only a little spreading under the oxide film. III type is the tunneling type. This kind of tunneling is very like that occurred in the specimens of as received state. That is, some gases evaporate simultaneously in the process of tunneling and the speed of tunneling is not so high. IV type is also one kind of tunneling phenomena. But in this case, the speed of tunneling is much higher than III type, and no gas evaporation is observed. However, some cracks are observed on the surface of oxide film. In the Fig. 13, in the first group (grinding and boiling) all specimens belong to IV type except one which is without the boiling treatment.

In the second group (chemical etching and boiling), the specimens, which were boiled less than 20 sec, belong to II type. The specimens boiled more than 30 min belong to I type. Other specimens belong to III type. In the third group, all the specimens belong to II type. In some specimens of III type, there is a cavity on the bottom side as shown in Fig. 15 (b). It seems at first there is the





(a) II type in Fig. 14

(b) III type in Fig. 14

Fig. 15 Shape of bottom side of some specimens after testing

erosion process and after tunneling the liquid of eroded part was drawn by tunneling flow. And the specimens of II type usually give the convex surface on the bottom side as shown in Fig. 15(a). It seems there is only the erosion process. The upper surface of the specimens of III type was observed by SEM. The typical blow hole on the surface of specimens is shown in Fig. 16. The center part

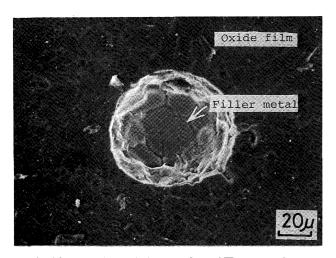


Fig. 16 Typical blow hole on surface of III type specimen

of the hole is the filler metal and the surrounding part of the hole is aluminum oxide film. This figure also shows that filler metal flows under the oxide film. Fig. 17 is the typical surface conditions (oxide film) of the specimens for IV type, and the filler metal only may exist under these oxides.

From the results of the experiment, we find that tunneling area varies with treatment time and there are

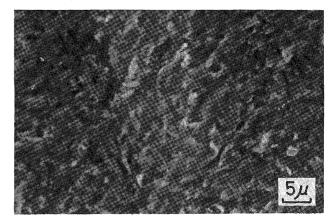


Fig. 17 Surface of IV type specimen

max. points in the first and second groups of tests. (See Fig. 13) It seems that metal/oxide interface of these specimens varies with the treatment time. The report of H. Yamada⁷⁾ gives us the curve of the thickness change of boehmite film in deionized water with boiling treatment time as shown in Fig. 13. The curve shows the thickness of film increases rapidly in the first stage (from 0 min to 5 min), after that, the rate of increasing of the thickness (from 5 min to 60 min) becomes smaller. In comparison of the results of the second group with the thickness change curve given by H. Yamada, there is some relationship between the oxide film formation process and the tunneling area. When the treatment time is less than 5 min, the thickness of oxide film changes very rapidly and the tunneling area also increases very evidently. When the boiling time is more than 5 min, the thickness of oxide film increases more slowly and the tunneling area decreases with the increase of the treatment time. It seems that, in the first stage of oxide formation, the interface of metal and oxide is more unstable, that is, the space distribution of electron charge in this stage may be more unbalanced.8) In this condition of the interface, Si of filler metal may be easier to diffuse along the interface. After long time boiling, perhaps, the structure of metal/oxide interface gradually changes to more stable state. So that the diffusion of Si along the interface becomes unfavorable and the tunneling area decreases with treatment time. In the first group, specimens were polished by emery paper, so that the degree of the unbalance at metal/oxide interface may be severer than that of the second group. So, the tendency of the tunneling is also higher than the second group. According to the reports⁶).8), oxide film in air at low temperature is not uniform and it is weak also, so that, we can presume that this kind of oxide film and metal/oxide interface are not suitable for tunneling flow, and the tunneling process is very easily to be stopped. All the specimens of the third group and some specimens of the second group with very

short treatment time gave the results in II type. These phenomena may be explained with the above mentioned point of view. After tunneling process, the specimens of the second group and the specimens of as received state had blow holes on the surface of the tunneling phenomena. It seems many gases evaporate in the tunneling process. According to the report of H. Yamada⁷, oxide film and metal/oxide interface formed in boiling water may contain H₂O and H₂ gas. So that the gases evaporated in the process may be considered as H₂ gas.

4. Conclusion

The tunneling flow of filler metal (Al-12%Si, BA4047) along metal/oxide interface in aluminum brazing was studied with pinprick and with flux. Several interesting results were obtained as follows:

- (1) In spreading test of the filler metal on aluminum (1100) plate, tunneling flow can be obtained for following state of specimens.
 - (a) By pinpricking or by using mixed flux of chloride and fluoride for specimen of as received state
 - (b) By pinpricking for specimens chemical etched and boiled in deionized water with time interval from 20 sec to 30 min
 - (c) By pinpricking for specimens polished (or ground) with emery paper and boiled in deionized water for no less than 20 sec

Tunneling area varies with treatment time and has a maximum at boiling time of $4 \sim 5$ min.

(2) Tunneling flow occurs when the ratio of ordinary spread area to the oxide removed area is bigger than unity. If this ratio is much smaller than unity, only ordinary spread can take place.

- (3) In tunneling process occurred in specimens of (1)-(a) and (1)-(b) series, a lot of gases evaporate simultaneously. And the tunneling speed is not so high. The tunneling process of (1)-(c) series gives no impression about gas evaporation, but some cracks are observed on the surface of oxide film. Tunneling speed of this type is much higher than that of the former type.
- (4) The tunneling flow can not be obtained under every type of aluminum oxide film on base metal. The growth mechanism of tested oxide films may relate to the mechanism of tunneling flow.
- (5) The tunneling flow can be used to evaluate the oxide removability of fluoride flux. The higher the removability, the larger the non tunneling area can be detected by described method.

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