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Studies on Vacuum Brazing (Report I)[†]

— Removing of oxide film from carbon steel surface and brazing alloy spreading mechanism —

Yoshiaki Arata*, Akira Ohmori and Cai Huai Fu*****

Abstract

Vacuum brazing of carbon steels was studied both on the removal of oxide film from carbon steels (S45C, S25C, Armco Fe)surface and brazing alloy (BAg—8b) spreading mechanism. This research was done in order to clarify the relation between the removing oxide film and decarborizing phenomenon, which occur by heating various oxidized carbon steels in vacuum. Moreover, the brazability was checked by spreading test on carbon steel surface, and oxidation, decarborizing and spreading phenomena were investigated.

It was shown that, the decarborizing of carbon steel caused by heating in vacuum was promoted by the existence of oxide film on the specimen surface. This phenomenon for high carbon steel (S45C) was brought about more easily than for low carbon steel Armco Fe. Spreading is due to the primary diffusion of Cu of brazing alloy into grain boundary grooves formed on carbon steel surface by removal of oxide film during vacuum heating with carbon. Furthermore, it was determined that the activation energy for spreading of molten BAg—8b on polished surface is 44.2 kCal/mol and 24kCal/mol on oxide surface of steel(S45C).

KEY WORDS: (Vacuum Brazing) (Spreading) (Mechanism) (Oxidation) (Carbon Steel) (Silver Alloy) (Surface treatment)

1. Introduction

Vacuum brazing is one of the best joint methods, whether joining the same materials or different materials. Therefore vacuum brazing have been employed as a substitute for other brazing methods, which are expensive for brazing with fluxes and are very difficult to remove residual fluxes in brazing joint after brazing. Particularly, vacuum brazing is necessary for some materials, which can not be brazed by furnace brazing with inert gas.

One of the most important phenomena associated with vacuum brazing process is spreadability of brazing alloy on base metal. In usual case the surface of base metal on which oxide film exists, can not be wetted by brazing alloy. Nevertheless, the oxide film can be removed from surface of base metals during vacuum brazing and then liquid brazing alloy can easily spread on the surface of base metals.

There are many published paper on the study of spreading mechanisms concerning with vacuum brazing. Often, a halo (a band of reaction between brazing alloy components and substrate) is seen ahead of a spreading droplet(1) and the primary diffusion of copper within brazing alloy was reported(2), but no paper was known about the grain boundary groove on the surface of carbon steel. Tunneling theory was suggested(3)(4) to describe the mechanism of penetration of brazing alloy through the oxide film—base metal interface. Chemical removal of oxide film on copper by phosphorous—rich liquid was also found[5)]. After puncturing the oxide film, the surface of base metal can be wetted with liquid brazing alloy[3) 4)]. The activation energy for speading of brazing alloy (BAg—8a) on carbon steel is 41.1Kcal/mol and is independent on the carbon content in carbon steel[6)]. As described above, the spreading mechanisms are rather complicated and they are different for brazing alloy—base metal systems. So, up till now, there has not been any unified theory and many phenomena remain unclarified.

Present study was done on the effect of carbon content on the removing of oxide film in various carbon steels during vacuum heating and on the spreading phenomena of brazing alloy (BAg—8b). Spreading phenomena of brazing alloy on the surface of carbon steels with different surface treatments were discussed. Particularly, the promotion effect of spreading by the existence of oxide film on surface of carbon steels and the effect of carbon content on the spreading were noticed. Consequently, the spreading mechanism of brazing alloy on the surface of carbon

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steels was clarified.

2. Specimens and Experimental Procedure

In this experiment, chemical compositions of carbon steels used are shown in **Table 1.** Specimens were in 18mm diameter and of 2mm thickness. The surface of specimens was polished with emery paper and was degreased with acetone.

Experimental apparatus is shown in **Fig.1.** Vacuum heating treatment and spreading test was done under 2 x 10^{-5} Torr(about 2.67 x 10^{-3} Pa).

A change of surface state of steels in vacuum heating was observed by high temperature optical microscope. The change of surface state and front edge of spreading droplet was observed by SEM. Behaviour of chemical elements was analyzed by EDX. Ag–28Cu–0.5Ni (BAg–8b) was used as brazing alloy.

Table 1. Chemical composition of carbon steels.

Chemical composition (wt %)					
Material	C	Si	Mn	P	S
S45C	0.47	0.23	0.66	0.02	0.019
S25C	0.28	0.22	0.45	0.02	0.024
Armco Fe	0.028	0.004	0.007	0.003	0.001

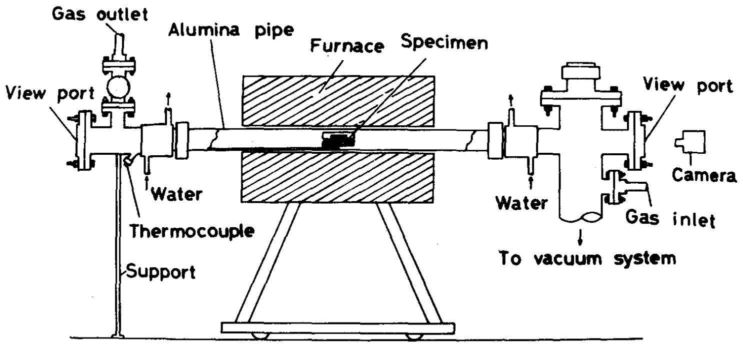


Fig 1. Schematic Diagram of Apparatus.

3. Experimental Results and Discussion

3.1 Effect of carbon content on growing and removing of oxide film.

At first the effect of heating temperature and time under atmosphere on formation of oxide film on carbon steels was examined. The effect of the heating temperature(oxidation time 1 hr) on weight gain is shown in **Fig.2. Fig.3** shows the heating time dependence of weight gain at 500°C. The time dependence of weight gain was conformed to the parabolic law so that

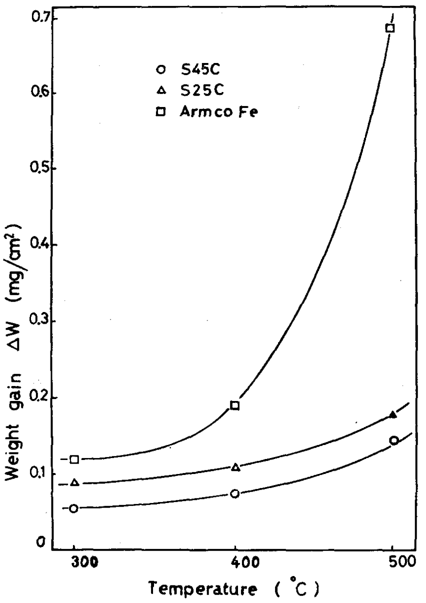


Fig 2. Oxidation temperature dependence of weight gain.

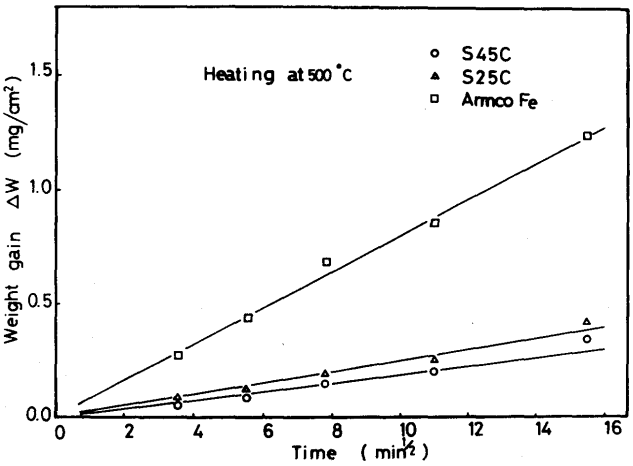


Fig 3. Oxidation time dependence of weight gain.

the following equation might be derived,

$$\triangle W = k \cdot t^{\frac{1}{2}} \qquad (1)$$

where, $\triangle W$ is the weight gain,t is heating time, k is the reaction rate constant for the growing of oxide film.

Fig.4 shows SEM results of oxide layer of various carbon steels after 4hr x 500°C heating under atmosphere. It can be noticed that weight gain increases proportionally with heating temperature and heating time, but the increment is less for high carbon steel than for low carbon steel due to the simultaneous reduction of oxide film by the carbon in the steel during the heating process. From x–ray diffracton analysis, such oxide film is composed mainly of Fe_2O_3, Fe_3O_4 and small amount of FeO.

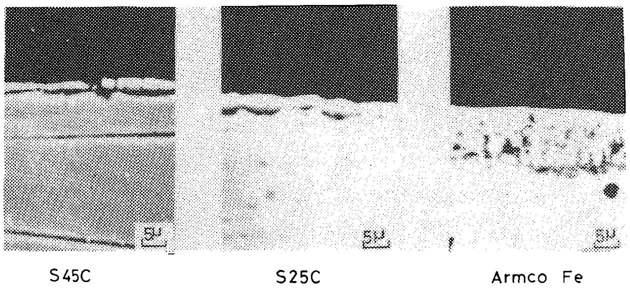


Fig 4. Oxide layers of carbon steel after oxidation for 4hr at 500°C.

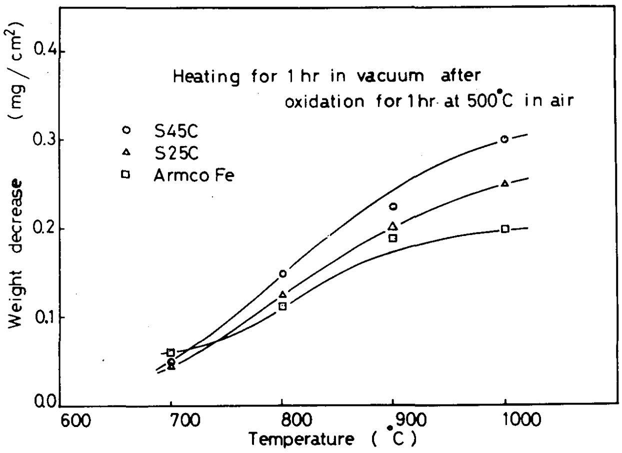


Fig 5. Vacuum heating temperature dependence of weight decrease.

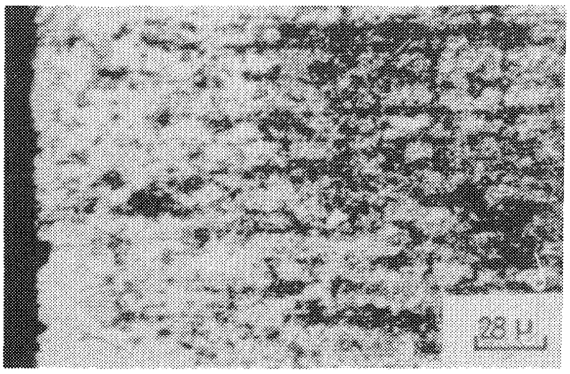


Fig 6. Decarborization layer of S45C after Vacuum heating.

The effect of carbon content in carbon steel on growing and removing of oxide film was noticeable and the effect of such a surface state change on brazability is very important in vacuum heating. **Fig.5** shows the effect of vacuum heating temperature on weight decrease after oxidation treatment under atmosphere for lhr at 500°C. From Fig.3 weight gain is 0.7 mg/cm^2 for Armco Fe, 0.2mg/cm^2 for S25C, and 0.15mg/cm^2 for S45C respectively for oxidized carbon steels under air atmosphere for lhr at 500°C. However, Fig.5 shows that for specimens of S45C with oxidation treatment for lhr at 500°C, their weight decrease is 0.25mg/cm^2 after vacuum heating for lhr at 900°C, but for specimen without oxidation treatment, their weight decrease is only 0.05mg/cm^2. It is considered reasonable that the weight decrease of oxide film is due to reduction by carbon as indicated in the following eqation

$$MO + C \rightarrow M + CO \qquad (2)$$

So, the weight decrease by vacuum heating treatment is larger for the specimens with oxidation treatment. Also the reduction effect of carbon for removing oxide film is more noticeable in high carbon steel. And decarborization phenomenon of carbon steel surface after vacuum heat treatment was confirmed. **Fig.6** shows one of the examples of surface decarborization phenomenon of S45C steel with oxidation treatment for 15min at 500°C.

From Fig.2 and Fig.5 it is known that the removal of oxide film is easy for S45C steel with 1 hr oxidation treatment at 300°C or 400°C by such a vacuum heating but such removal is not the case with S45C steel after 1 hr oxidation treatment at 500°C.

3.2 Spreading phenomena on differently treated surfaces of carbon steel

The removing of oxide film on carbon steel in vacuum heating is greatly affected by the carbon content of steel and the thickness of oxide film. The effect of both a kind of carbon steel and such a surface oxidation state on spreading is also noticeable during vacuum brazing. **Fig.7** shows the results of spreading test of BAg–8b brazing alloy for 3 min at 840°C on various oxidation treated surfaces for S45C steels. From Fig.7 it can be noticed that spreading area is almost the same for polished surface and for either 100°C or 200°C oxidation surface. But it is significantly increased for the oxidation treated surface at 300°C. However, spreading process was constricted

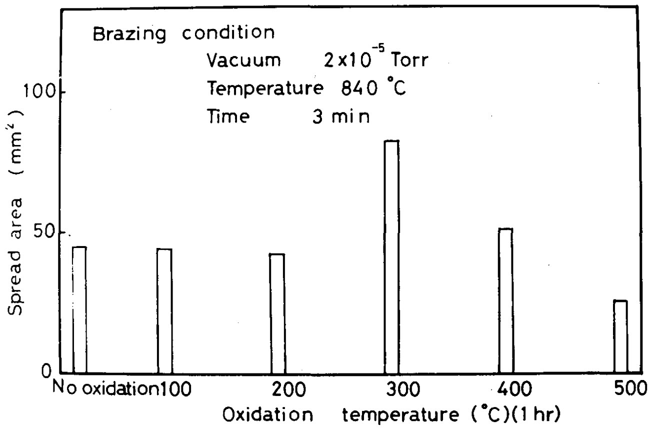


Fig 7. Oxidation temperature dependence of spreading area.

for the oxidation treated surface after oxidation treatment at 500°C.

Spreading behavior for polished surface and oxidation treated surface (300°C) is different. The spreading state for the oxidation treated surface may be divided into two regions, S_{I} and S_{II}, as shown in **Fig.8.** In order to clarify more the spreading phenomena of oxidated surface, various carbon steels were spread and the results are shown in **Fig.9**. There is a great difference between high carbon steels(S45C,S25C) and low carbon steel(Armco Fe) for oxidated surface at 300°C or 400°C. The spreading area on oxidized surface for the high carbon steels especially S_{II} increases significantly in comparison with low carbon steel. Moreover the increament of spreading area is due to significant increase of S_{II} for oxidated surface at 400°C. However, it is obvious that the spreading area increases with heating time at each heating temperature. But for oxidated surface at 500°C the spreading area is pretty small for all the carbon steels.

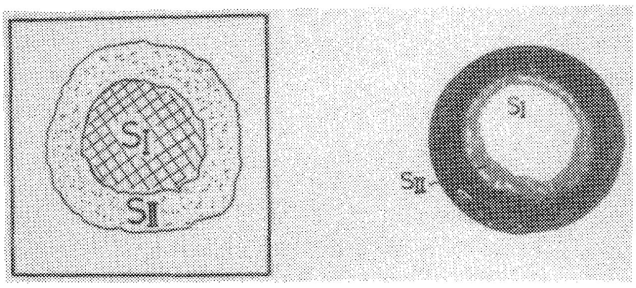


Fig 8. Spreading states for oxidation surface.

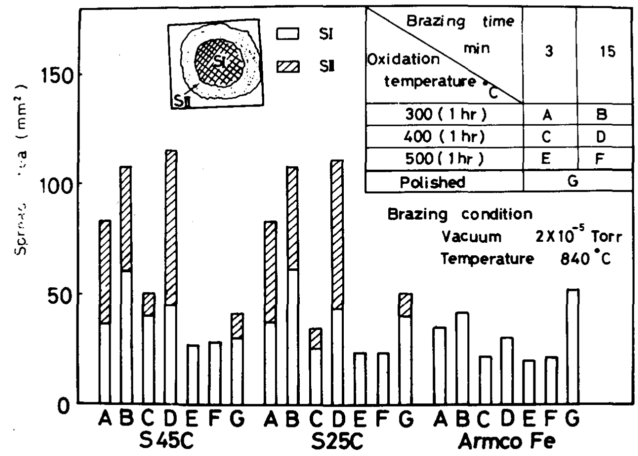


Fig 9. Spreading of brazing alloy on oxidation surface.

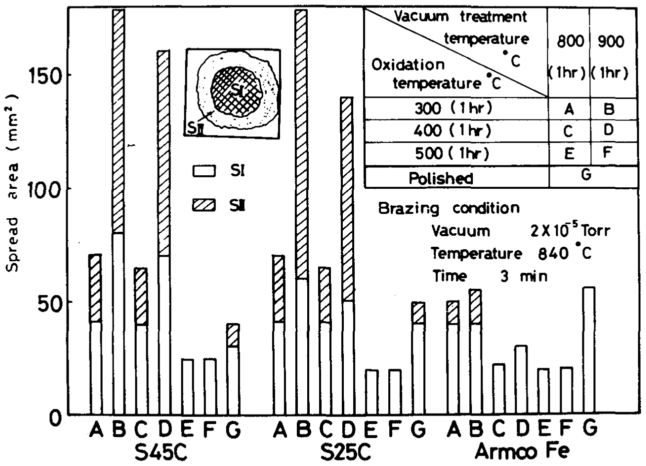
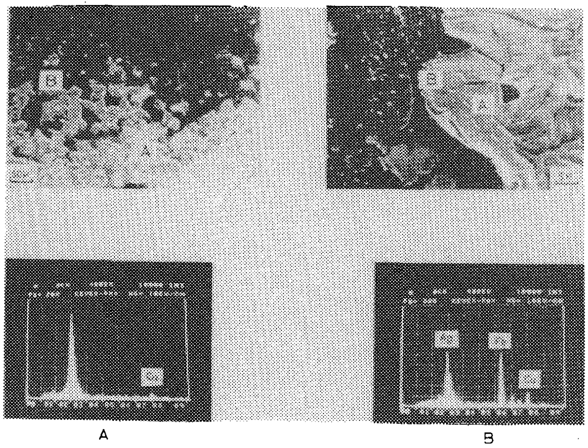


Fig 10. Spreading of brazing alloy on vacuum heat treated surface.

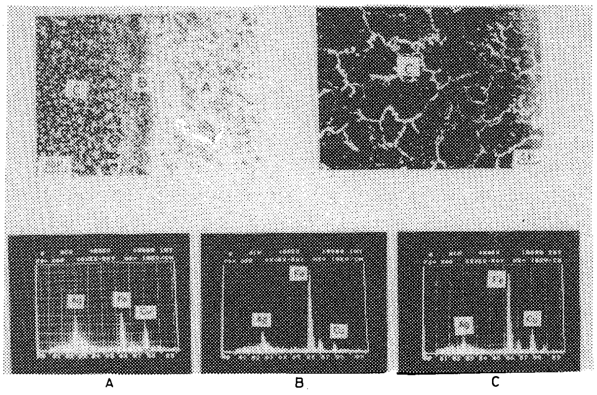
Fig.10 is the test results of spreading area for vacuum heat treated surface (at 800°C or 900°C) of various carbon steels after oxidation. From Fig.10 It may be observed that for vacuum heat treated surface the spreading area after 900°C treatment is larger than after 800°C treatment.

3.3 Spreading mechanism in vacuum brazing

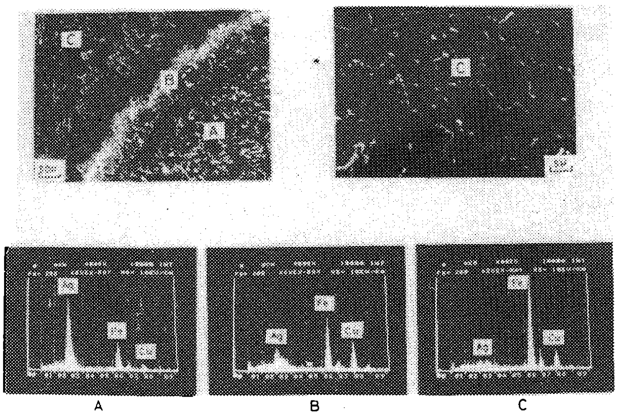
From the foregoing, it can be seen that the spreading may be promote in vacuum brazing when oxide film exists on the surface of higher carbon steel. Furthermore, spreading area is dependent on the carbon content in carbon steel, brazing temperature, brazing time, thickness of oxide film and etc. A existence of oxide film promotes especially the increase of spreading area S_{II} on the surface of carbon steel. **Fig.11** shows the micrograph of the front—end of spreaded brazing alloy by SEM and the distribution of chemical elements at the front—end of spreaded brazing slloy by EDX. From this figure, one important characteristic was confirmed that grain boundary grooves on the oxidation treated surface were impregnated with Cu—rich liquid of silver brazing alloy at the front—end of spreaded brazing alloy. Contrarily, this phenomenon was not found on the polished surface. Furthermore, by the analysis of EDX, the decrement of Ag/Cu ratio was confirmed from the middle to the edge of the spreaded brazing alloy, that is to say, copper is richer at the front—end of the spreaded brazing alloy for oxidation treated surface. But this phenomenon can not be found for spreading on polished surface and chemical composition of BAg—8b brazing alloy kept unchanged. From the above stated, the followings are clarified: Grain boundary grooves were formed on the surface of base metal during removing of oxide film by the reduction by carbon in carbon steel and there are so much Cu—rich alloy or even Cu in the grain boundary grooves. Cu—rich or Cu diffuses easily along these grooves, and then liquid brazing alloy can spread over this surface filled partly with Cu—rich or Cu. On the contrary this phenomenon can not be found on polished surface. The removing of oxide film and the change of surface state were



Spread state of polished surface



Spread state of oxidation surface for S45C (300 °c 1 hr)



Spread state of vacuum treatment surface for S45C
(800 °c 1 hr after oxidation for 1 hr at 300 °c)

Fig 11. Micrograph of spreaded surface and distribution of chemical elements.

observed by high temperature optical microscope during heating. A part of the microphotographs are shown in **Fig.12**. From Fig.12, the removing of oxide film was started from near region of grain boundary of carbon steel surface about 650°C for oxidation treated surface at 300°C or 400°C, and then the grain boundary grooves grew up on all surface at 750°C. But these grooves were not found on the surface of low carbon Armco Fe under the same condition, because carbon is easy to diiffuse from inside to surface along grain boundary of high carbon steel and then oxide film was reduced by carbon here. **Fig.13** shows the schematic model for removing process of the oxide film and growing of grain boundary grooves. Herefrom, the spreading mechanism of brazing slloy on oxidation surface may be described as following. First, oxide film is removed from grain boundary on the surface by carbon and then grain boundary grooves are produced on the surface about 750°C. Copper in silver brazing alloy is easily diffused along the grain boundary grooves. So spreading of silver brazing alloy liquid is easily to make progress on the surface filled partly with Cu—rich alloy or Cu. S_{II} spreading area is easily to grow up due to the diffusion of Cu—rich or Cu of silver brazing alloy along grain boundary grooves. However, S_{II} spreading area is very limited for the polished surface and the diffusion of copper of silver brazing alloy along grain boundary grooves was not found. Then, S_{I} spreading area only is recognized for both polished surface and the surface oxidized for lhr at 500°C.

Usually, there exists a linear relation between the square of spreading area and heating time at each heating temperature⁶⁾. From the present study, the relation between the square of spreading area and the heating time for both polished surface and oxidation surface is shown in **Fig. 14 (a) (b)**. The heating time (t) was defined as O when the heating temperature reached the predetermined brazing temperature. So the spreading area (S) was defined as So by drawning the straight—line to terminate the ordinate as shown in the figure. Relation between the spreading area S and heating time t may be expressed as the following equation:

$$S^2 = S_0^2 + Kt \tag{3}$$

where, K is a spreading coefficient.

From Fig.14(a)(b), it can be observed that So at each temperature for oxidation surface is larger than So for polished surface. Comparing Fig.14(a) with Fig.14(b), it can be noticed that up to 870°C K value for oxidation surface is larger than the value for polished surface and both values becomes about same values at about 900°C. This is due to the growing of grain boundary grooves which were impregnated by liquid brazing alloy on the polished surface about 900°C similar to the oxdation surface.

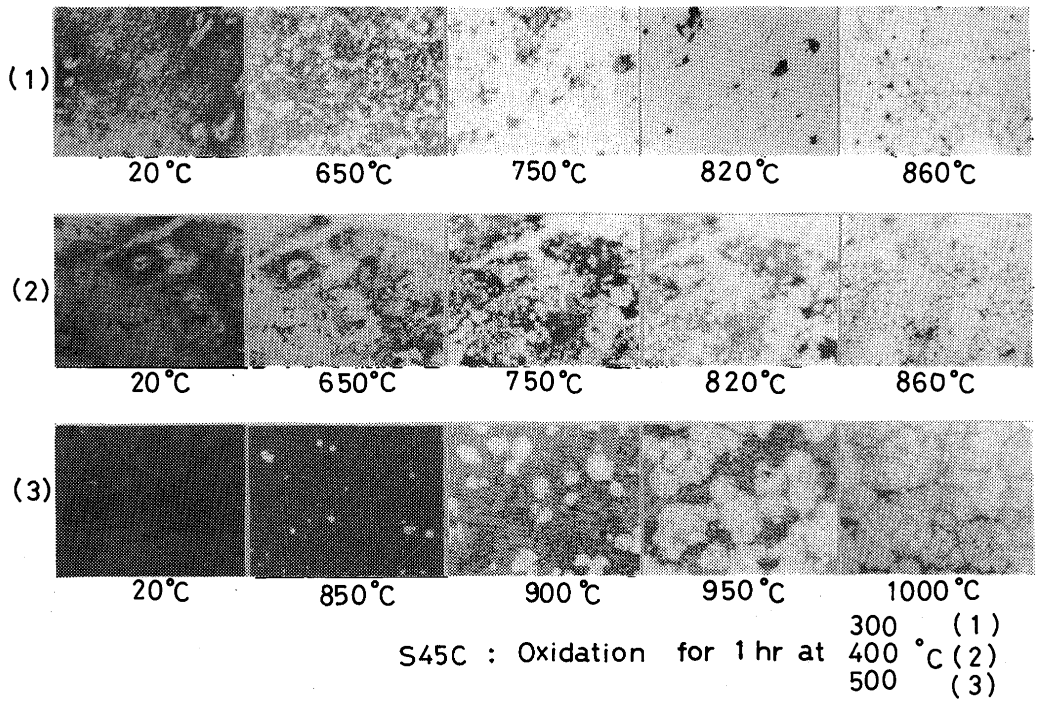


Fig 12. Change of oxidation surface during vacuum heating.

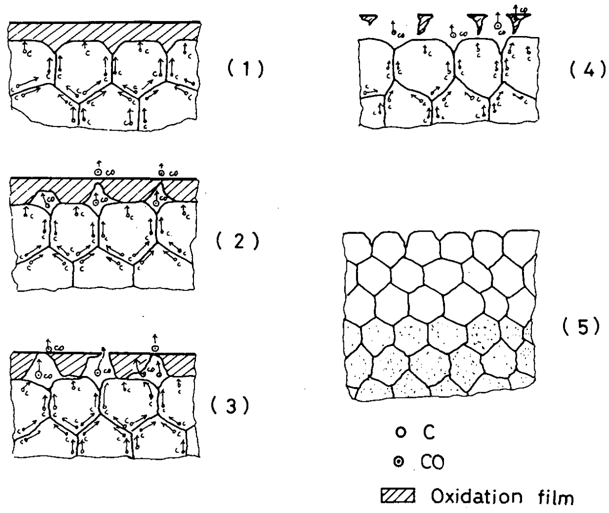


Fig 13. The schematic model of the oxide film removement process.

The spreading coefficient K, as a function of absolute temperature T, may be expressed as follows:

$$K = Ko \cdot \exp(-Q/RT) \qquad (4)$$

where Ko is a constant.

Q is activation energy for spreading.

R is the gas constant.

The relation between Log K and 1/T was plotted in **Fig.15**. Therefore, the activation energy can be calculated from Fig.15. The activation energy for spreading of BAg–8b on the polished surface (S45C) is about 44.2 Kcal/mol, and about 24 Kcal/mol for spreading of BAg–8b on the oxidation surface(S45C).

The Q value for spreading of BAg–8b on the polished surface in this experiment agrees with the data given by Kawakatsu6) et al. But activation energy Q for oxidation surface is less than Q for the polished surface. The spreading rate is larger due to the primary diffusion of Cu or Cu–rich alloy along grain boundary grooves. The activation energy for spreading on S25C steel surface is almost the same as the value for S45C steel. However, the activation energy for spreading on Armco Fe surface is not lowered by oxidation treatment. The important effect of carbon on both spreading of brazing alloy and removing of oxide film in vacuum brazing was confirmed.

4. Conclusions

The results of these investigations are summarized as follows:

(1) Spreading of silver brazing alloy BAg–8b was promoted by the existence of oxide film on the surface of carbon steel and the effect of carbon content and thickness of oxide film on both spreading process and removing process is noticeable.

(2) Spreading mechanism of silver brazing alloy (BAg–8b) on oxidation surface for high carbon steel (S45C, S25C) is as follow: oxide film is firstly removed from grain boundary of steel surface by carbon and then grain boundary grooves are produced on the surface. So copper of silver brazing alloy easily

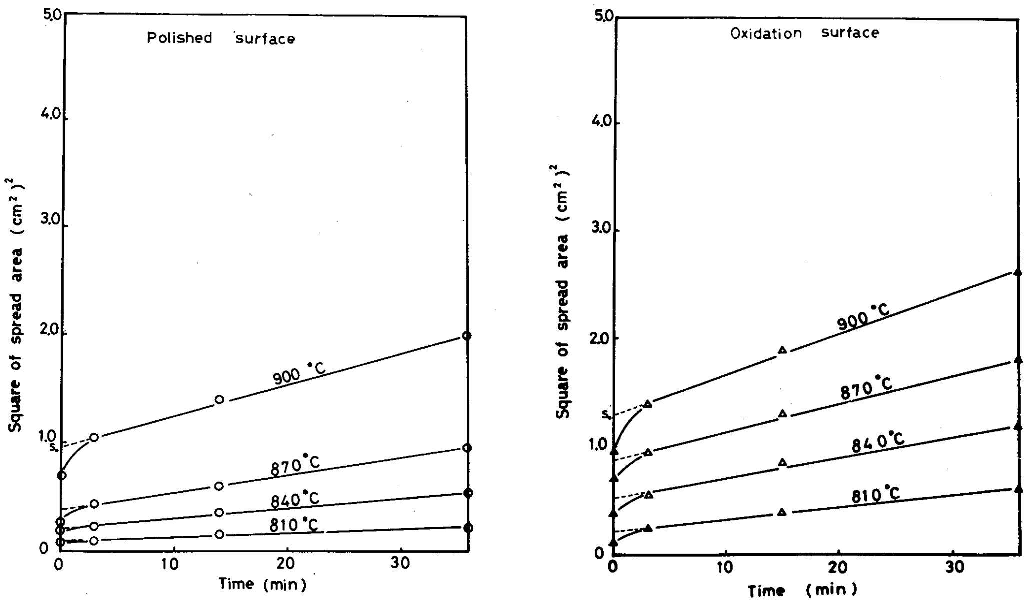


Fig 14. Relation between the spreading area and heating time.

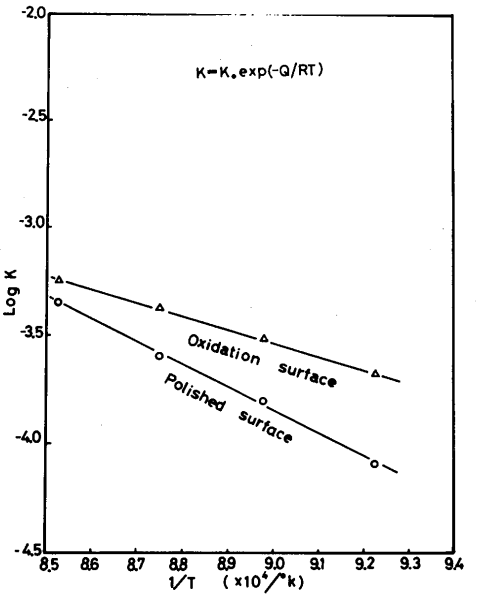


Fig 15. Relation between Log K and 1/T.

diffuses along grain boundary grooves. Consequently, the spreading of silver brazing alloy liquid is easily to make progress on the surface filled partly with Cu—rich alloy and Cu.

(3) The spreading area of silver brazing alloy on carbon steel tends to increase parabolically with heating time at each temperature. The activation energy for spreading of molten BAg—8b is 44.2 Kcal/mol on polished surface of carbon steel(S45C) and is 24 Kcal/mol on its oxidation surface. The surface state of carbon steel affects greatly the activation energy for spreading of brazing alloy.

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