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Effect of Halogenation Treatment to Solder on Anodic Soldering[†]

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Abstract

The effect of the halogenation treatment of tin based solder on the wettability of tin based solder to glass was examined, and that treatment was applied to anodic soldering - soldering of glass utilizing the principle of anodic bonding. The halogenation treatment by hydrogen chloride vapor considerably improves wettability of pure tin solder and Sn-3.5mass%Ag solder to glass. In anodic soldering, the halogenation treatment improves the spread of solder at the joint interface. In anodic soldering using pure tin solder receiving the halogenation treatment, application of voltage improved the strength of produced joints. But too long application of voltage was harmful to soundness of the joints. This was thought to be caused by excess growth of the oxide layer at the joint interface. In soldering using Sn-3.5mass%Ag solder, the effect of the voltage application was not clear.

1. Introduction

Anodic bonding is a method for bonding metals or semiconductors to glass containing alkali ions by applying a D.C. voltage of 100-1000 V between them with the metal side anodic at a bonding temperature of 500-700 K. In this temperature range thermal diffusion of alkali ions in glass is activated, and under the influence of the electric field induced by applied voltage, these ions drift toward the cathode side, and an alkali ion depletion layer forms in the glass near the joint surface. This layer has a strong negative charge because of the presence of non-bridging oxygen (O) anions that lose their bonds with the alkali ions. A Coulomb force acting between this charge and the charge appearing on the surface of the anode conductor brings the glass and the conductor into intimate contact, and a permanent bond is achieved by the reaction of oxygen from the glass with elements in the conductor at the interface [1].

Anodic bonding achieves direct bonding of conductor to glass without intermediates such as solder or adhesive, and the bonding temperature of this method is low enough not to cause deformation of the glass [2]. Because of these features, the major application of anodic bonding is the precise bonding of semiconductor (silicon in most cases) to glass, used in the assembly of MEMS devices or microcapillaries, for example. But the principle of anodic bonding described above can also work on the combinations of liquid conductors and glass. Soldering of glass needs metallizing of glass as a preprocessing

because of poor solder wettability of glass [3]. If an anodic bonding voltage is applied to molten solder and glass substrate, the Coulomb force that acts between the surfaces of molten solder and glass may improve intimate contact of solder and glass. This effect may lead to a new soldering process of glass that does not need metallizing of the glass - i.e. anodic soldering.

There is a factor that can prevent successful anodic soldering. The surfaces of tin or tin based solder are covered with robust tin oxide layers. These layers often cause problems soldering because that they prevent wetting of joint materials by the solder. It was reported that the halogenation treatment – exposing the surface of the solder to hydrogen halide gas improves joinability of tin in diffusion bonding [4,5]. With this treatment, a portion of oxygen in the oxide layer is replaced with halogen. This reaction breaks oxygen bridges and weakens binding of the layer. If the halogenation treatment makes it easy to disperse tin oxide layer on the surface of the solder, it may be effective in improving wettability of the solder.

In this study, the effect of halogenation treatment on the wettability of tin based alloy to glass was examined, and anodic soldering using solders receiving the halogenation treatment was tried. Kovar alloy and borosilicate glass were soldered using pure tin solder and Sn-3.5mass%Ag solder that had received the halogenation treatment by halogen chrolide vapor. An anodic bonding voltage was applied to the molten solder and glass in the process of soldering. Effect of the voltage

application was evaluated from appearances and shear strength of the joints.

2. Experimental

Kovar alloy (Fe-29mass%Ni-17%Co alloy) and borosilicate glass Corning 7056 were adopted as the joint materials. Corning 7056 glass has a thermal expansion coefficient similar to that of Kovar alloy, and is widely used in glass-metal joints. The glass was provided as disks of 1 mm in thickness and of 25 mm in diameter, and Kovar alloy was fabricated as disks of 3 mm in thickness and 16 mm in diameter. The faying surfaces of the glass and Kovar alloy disks were finished by mechanical polishing and buffing. Foils of pure tin and Sn-3.5mass%Ag alloy (Sn-3.5Ag) were used as solder in this study. The Sn-3.5Ag foils were 30 μm thick. The pure foils 30 μm and 50 μm thick were used in order to observe the effect of the thickness of the solder on performance of the joints. The solder foils were cut into pieces 10 mm square.

The glass disk and Kovar alloy disk were soldered as follows. The schematic illustration of the soldering apparatus is shown in **Fig. 1**. The glass disk was laid on the copper negative electrode plate. The surface of the glass that contacted the electrode plate (the surface NOT to be joined with the Kovar alloy) was coated with conductive carbon paint in order to apply a uniform voltage to the surface. A solder piece was put on the faying surface of the glass. The halogenation treatment was applied to the solder pieces just before use. The Kovar alloy disk was put on the solder. The Kovar alloy disk was connected to the positive electrode. The atmosphere in the specimen chamber was replaced with pure argon. The pressure of the argon gas charged into the chamber was 0.12 MPa at room temperature. The joint materials and the electrodes were heated to the bonding temperature by the surrounding carbon heaters. The temperature of the joint materials was estimated by monitoring the temperature of the dummy specimen that was put next to the joint materials. The temperature of the joint materials were raised to the destination in 3900 s. After that, a bonding voltage of 500 V was applied to the joint materials. Time for voltage application was varied in the range from 0 s to 7200 s. After application of the voltage, carbon heaters were turned off, and the joints
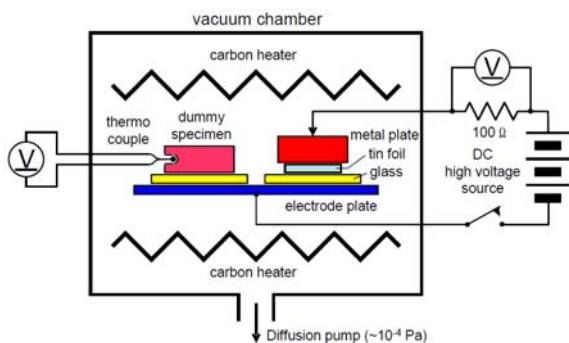
were cooled to room temperature in the chamber.

The halogenation treatment was applied to the solder pieces in the following way. A petri dish filled with concentrated hydrochloric acid was put in an airtight box. Air in the box was saturated with the vapor of hydrogen chloride evaporating from the dish. The solder piece to be was enclosed in the box quickly, and exposed to the hydrogen chloride atmosphere for 180 s. After the treatment the solder piece was set in the pure argon gas in the specimen chamber of the soldering apparatus with other joint materials as quickly as possible, and insulated from oxidizing atmosphere.
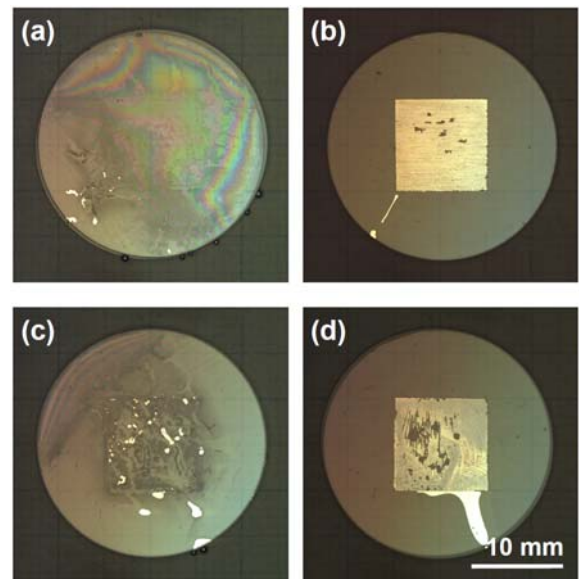
Conditions of joint interfaces of produced joints were investigated by appearance inspection through the transparent glass, and strength of the joint interface was examined by a shear test.

3. Results and Discussions

The effect of the halogenation treatment on wettability of the solders to glass was examined prior to the anodic soldering experiments. The pure tin and Sn-3.5Ag solder pieces receiving the halogenation treatment were inserted between pairs of glass disks, and heated to 623 K in 4500 s in an atmosphere of pure argon. Similar experiments using the solder pieces without the halogenation treatment were also done for comparison. In **Fig. 2** are shown the appearances of the solder after cooling observed through the glass. Without application of the halogenation treatment, most of the solders ran off during heating and did not remain in the gaps between glass disks (Fig. 2(a): Pure tin, Fig. 2(c): Sn-3.5Ag). Wettability of solders without halogenation treatment was poor and molten solders were repelled. On the other hand, solders that received the halogenation treatment kept their

Fig. 2 Behavior of solders that were inserted between glass disks. Pure tin, as-received (a), pure tin, receiving the halogenation treatment (b), Sn-3.5Ag, as-received (c), and Sn-3.5Ag, receiving the halogenation treatment (d).

Fig. 1 Schematic illustration of apparatus for anodic soldering.
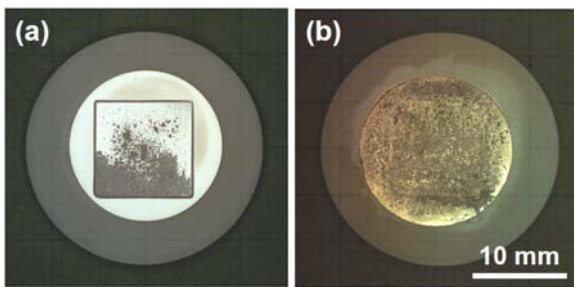
Fig. 3 Appearance of glass/solder interface in glass/Kovar alloy joints anodically-soldered at 623 K with application of a voltage of 500 V for 600 s using as-received pure tin solder (a), and that soldered at 623 K with application of a voltage of 500 V for 1000 s using pure tin solder receiving the halogenation treatment. (b).

original square shapes after heating (Fig. 2(b): Pure tin, Fig. 2(d): Sn-3.5Ag). The halogenation treatment improved the wettability of the solders to glass.

The halogenation treatment considerably improved the spread of solder in anodic soldering. Typical appearances of joint interfaces in anodically-soldered joints with and without the halogenation treatment are shown in **Fig. 3**. Without the halogenation treatment, spread of solders during soldering was limited and the solder pieces kept their original square shape partially after soldering (Fig. 3(a)). In contrast, solders receiving the halogenation treatment spread all over the joint interface (Fig. 3(b)). As mentioned above, when the solder not receiving the halogenation treatment was melted in a gap between glass and glass, it ran out of the gap. But in anodic soldering of glass to Kovar alloy, the solder was left at the joint interface. This is because the wettability of the solder to Kovar alloy is higher that to glass. Adhesion of the solder to the surface of Kovar alloy inhibited migration of the solder. The solders that received the halogenation treatment could wet both glass and Kovar alloy, and they could spread all over the joint interface by capillary action in anodic soldering. Soldering conditions (soldering temperature, voltage application time) were changed in certain ranges, but similar tendencies were observed regardless of these conditions.

Soldering conditions - the joining temperature, the voltage application time, the thickness of solder pieces, and chemical composition of the solder affected the performance of the produced joints. In each condition multiple joints were produced. In proper conditions all produced joints were sound, but in some other conditions occasionally joint interfaces of some produced joints were separated when the joints were cooled down. All separated joints fractured at the glass/solder interfaces. Improper soldering conditions resulted in weak glass/ solder interfaces, and those interfaces were sometimes broken by the residual stress that appeared during cooling after soldering. In **Table 1**, numbers of sound joints and broken joints are tabulated for each soldering conditions. At soldering temperature of 623 K, joints using pure tin solder 30 μm thick, Sn-3.5Ag solder 30 μm thick, and

Table 1 Conditions of Kovar alloy/glass joints anodically-soldered with application of a voltage of 500 V at 623 K using pure tin solder 30 μm thick (a), at 623 K using Sn-3.5Ag solder 30 μm thick (b), at 623 K using pure tin solder 50 μm thick (c), and at 673 K using pure tin solder 50 μm thick (d) catalogued with the voltage application time. Halogenation treatment was applied to all the solders.

(a)	0 s	480 s	1000 s	2400 s	7200 s
sound	3	3	5	2	-
broken	0	0	0	3	-

(b)	0 s	480 s	1000 s	2400 s	7200 s
sound	3	3	6	3	0
broken	0	0	0	2	3

(c)	0 s	1000 s	2400 s	3600 s	7200 s
sound	2	3	3	4	3
broken	0	0	0	0	1

(d)	0 s	220 s	480 s	1200 s	3600 s
sound	1	2	4	3	1
broken	1	1	0	1	3

pure tin solder 50 μm thick were produced. There was a tendency that too long voltage application times were harmful for the soundness of the joints. When solders 30 μm thick were used, joints broken just after cooling appeared with voltage application times of 2400 s or longer. When pure tin solder 50 μm thick was used, a broken joint appeared with a longer voltage application time, 7200 s. When the soldering was performed at 673 K using pure tin solder 50 μm thick, broken joints appeared all voltage application time except 480 s, and with voltage application for 3600 s, only 1 sound joint obtained by 4 trials. In the anodic soldering process (or in anodic bonding process in general), oxygen ions are provided to the joint interface from glass during application of the voltage. Oxidation of the anode surface by oxygen from glass is an essential process for completion of anodic bonding, but excess oxidation causes too much growth of an oxidation layer at the joint interface and can cause degradation of the interface. In **Fig. 4** the current that ran through the glass during the voltage application and the electric charge the current transferred are shown as functions of voltage application time. The amount of the transferred charge accumulated with time. In the glass, ions are the dominant current carrier, hence the charge amount represents the amount of oxygen ions that are provided to the joint interface. As seen in comparison between Fig. 4(a) and Fig. 4(b), a larger current ran through glass during the voltage application at higher temperature. Elevation of the temperature activates migration of ions in glass, and causes a decrease of electric resistance in the glass. These facts suggest a long application of the voltage causes a thick oxide layer, and a high soldering temperature causes quick growth of the oxide layer. Therefore, too long voltage application causes degradation of the glass/solder interface, and at higher soldering temperature, such change occurs quicker.
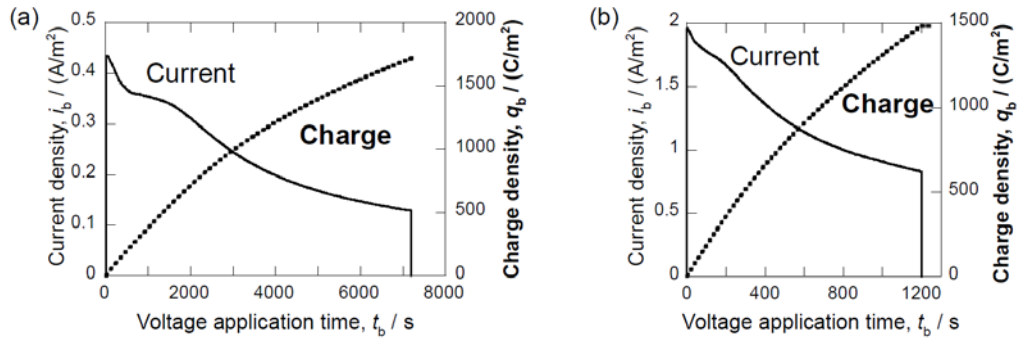
Fig. 4 Electric current that ran through the glass and charge that the current transferred during anodic-soldering of Kovar alloy to glass with application of a voltage of 500 V at 623 K (a) and 673 K (b) as functions of the voltage application time.

Strength of the joint interfaces was examined by the shear test. Values of shear fracture stress of joints are shown in **Fig. 5** as functions of the voltage application time. Glass is a brittle material, and joints of glass show unstable behavior in mechanical tests. So the data are widely spread. But for joints using pure tin solder (Fig. 5(a) and (b)), there is a tendency that the shear fracture stress increases with an increase in the voltage application time. And joints using solder pieces 50 μm thick showed higher shear fracture stresses than those of the joints which were soldered in the same condition using solder pieces 30 μm thick. Increase in strength of the joint interface with the voltage application indicates the improvement in intimate contact of solder to glass with voltage application. Improvement of strength with the use of thicker solder might be caused by the relaxation of the residual stress in thicker soft solder layer.

In the shear tests, all joints are broken at the solder/glass interface. White reaction product was observed sticking on the fracture surface of the glass side. The amount of the reaction product increased with the voltage application time. This product was thought to be oxide of tin.

When the Sn-3.5Ag solder was used, improvement in the joint strength with application of the voltage was not observed (Fig. 5(c)). The joint strength remained low value whether the voltage was applied or not. Silver is a element that has a high mobility in glass, and it is known that anodic bonding of silver to glass is difficult because Ag^+ ions that penetrate into the glass neutralize the negative charge in the alkali ion depletion layer in the glass. When the Sn-3.5Ag solder was used in anodic soldering, alloyed silver can penetrate into the glass and prevent intimate contact of solder to glass.
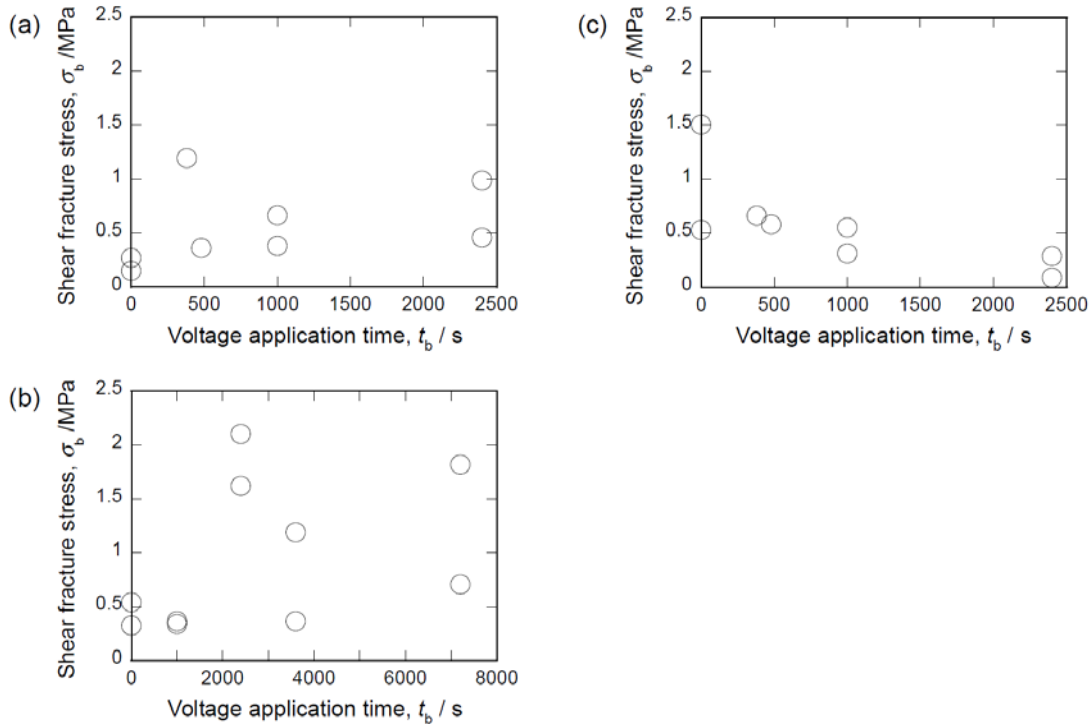
Fig. 5 Shear fracture stress of Kovar alloy/glass joints that were anodically-soldered with application of a voltage of 500 V at 623 K using pure tin solder 30 μm thick (a), at 623 K using pure tin solder 50 μm thick (b), and at 673 K using Sn-3.5Ag solder 30 μm thick (c) as functions of the voltage application time.

4. Conclusions

The effect of the halogenation treatment of tin based solder on the wettability of the solder to glass was examined, and application of the halogenation treatment to anodic soldering - soldering of glass utilizing the principle of anodic bonding was investigated. A summary of the results are listed below.

(1) The halogenation treatment considerably improves wettability of pure tin solder and Sn-3.5mass%Ag solder to glass.

(2) In anodic soldering, the halogenation treatment improves the spread of solder at the bond interface. It can be thought to be an effect of improvement in wettability of solder to glass.

(3) In anodic soldering using pure tin solder, application of voltage improved the strength of produced joints. But too long an application of voltage was harmful to soundness of the joints. In soldering using Sn-3.5Ag solder, effect of the voltage application was not clear.

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