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Materials

Effect of Kovar alloy oxidized in simulated N_2/H_2O atmosphere on its sealing with glass

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Abstract: The effect of Kovar alloy oxidized in simulated field atmosphere on its sealing with glass was studied in this article. After Kovar plates and pins were preoxidized in N_2 with 0°C, 10°C and 20°C dew points at 1000°C for different times, Fe_3O_4 and Fe_2O_3 existed in the oxidation products on Kovar surface, and the quantity of Fe_2O_3 increased with increasing dew point and oxidation time. Then they were sealed with borosilicate glass insulator at 1030°C for 20 min. The results indicated that the type and quantity of oxidation products would directly influence the quality of glass-to-metal seals. With the increase of oxidation products, gas bubbles in the glass insulator were more serious, the climbing height of glass along the pins was higher, and corrosion of Kovar pins caused from the molten glass was transformed from uniform to the localized.

Key words: Kovar alloy, oxidation, sealing, glass; microelectronic package

1. Introduction

Kovar alloy is widely utilized for matched glass-to-metal sealing in microelectronic packages, as its thermal expansion curve is accordant with that of hard borosilicate glass between 0-400°C [1]. But the glass does not wet on Kovar alloy, hermetic sealing is realized by bonding of molten glass with oxide film on Kovar alloy. In industrial practice, Kovar plates and pins should initially be decarburized and outgassed in wet hydrogen environment, then pre-oxidized in weak oxidizing atmosphere, and finally be sealed with glass beads in an inert atmosphere [2-4].

The oxidation behavior of Kovar alloy has been studied at 1000°C in N_2 atmosphere simulated field condition with 0°C, 10°C and 20°C dew points. The results indicated that Fe_2O_3 existed in the oxidation products on Kovar alloy besides Fe_3O_4, and the quantity of α-Fe_2O_3 would exceed that of Fe_3O_4 under the conditions of high dew point and long oxidation time [5]. The purpose of this article was to investigate the effect of Kovar plates and pins oxidized under the above conditions on the quality of seals with borosilicate glass insulator during the same sealing process. It was found that the seal quality almost depended on the type and quantity of oxidation products on Kovar alloy, and these will be significant to enhance the reliability of microelectronic packages.

2. Experimental

2.1. Experimental specimens

Kovar plates (30 mm × 15 mm × 1 mm) and pins (ϕ0.45 mm) used in this experiment were provided by a package factory with the reference HD-10, and the sealing glass was BH-G/K borosilicate glass beads.

2.2. Experimental procedure

Kovar plates and pins used in this study were first decarburized at 1050°C in N_2 saturated with water vapor at ambient temperature (about 25°C).

Then Kovar plates and pins were oxidized at 1000°C in N_2 with 0°C, 10°C, and 20°C dew points, and the oxidation time was 5, 10, 15, 30, 45, and 60 min, respectively. Each of the 18 groups had four parallel specimens.

In the following sealing step, the oxidized plates and pins and the preformed borosilicate glass beads were assembled in a graphite boat. Graphite boats

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were placed in a DSL-8 belt furnace, the high-temperature region in it was 1030°C and the belt speed was 30 mm·min^{-1}, so the residence time in the high-temperature region was about 20 min. The leakage tests of seals were carried out by ZQJ-230E helium mass spectrometer leak detector. The cross-sections of seals were examined by SEM. The pins were pulled out of the glass insulator with a WDS-5 microcomputer controlling tester, and then the surfaces of the pins were observed by SEM.

3. Results and discussion

3.1. Leakage test

The results of leakage tests indicated that the leakage rate of the above-mentioned seals was less than 1.0×10^{-9} Pa·m^3·s^{-1}, no matter before or after nickel electroplating, or after three cycles of 90° arc bending at the load of 0.83 N applied to the pins. Amongst these, better preoxidation conditions were at 1000°C for 5 min or 15 min with a dew point of 20°C, or at 1000°C for 5 min or 15 min or 30 min with a dew point of 10°C, or at 1000°C for 5 min with a dew point of 0°C. The above results were close to that of past researchers [6-8].

3.2. Cross-section analysis of seals

3.2.1. Gas bubbles in glass insulator

Fig. 1 shows the cross-section of seals which was obtained by Kovar plates and pins first oxidized at 1000°C for different times in N_2 with a 20°C dew point, then sealed with a borosilicate glass bead under the same condition. Many spherical substances with different sizes can be found in the glass insulator between pins and plates, and energy dispersive spectroscopy (EDS) analysis of these spherical substances showed no signals, which indicated these spherical substances were gas bubbles. As seen from Fig. 1, the size of gas bubbles increased with increasing oxidation time. Notis [9] considered that the main composition of gas bubbles was CO and CO_2, and the important reason was the presence of carbon in Kovar alloy. But all Kovar plates and pins used in this experiment were decarburized, oxidized and sealed with glass under the same condition, their unique difference was oxidation time, that is the differences of the type and quantity of oxide [5], so the differences of gas bubble in the glass insulator should be attributed to the types and quantities of oxides on the surface of Kovar alloy, and the specific mechanics will be published in the following article. And it is analogous to the gas bubble phenomenon when Kovar alloy was oxidized at 1000°C in N_2 with 10°C or 0°C dew point, the difference laid in the smaller size of gas bubbles as the dew point decreased.

3.2.2. Climbing height of glass along the pins

The climbing height of glass along the pins was measured from Fig. 1, and the relationship between glass climbing height and oxidation time is given in Fig. 2. It shows that the climbing height of glass along the pins increases with oxidation time in N_2 with the same dew point, and the climbing height also increases with dew point in the same oxidation time.

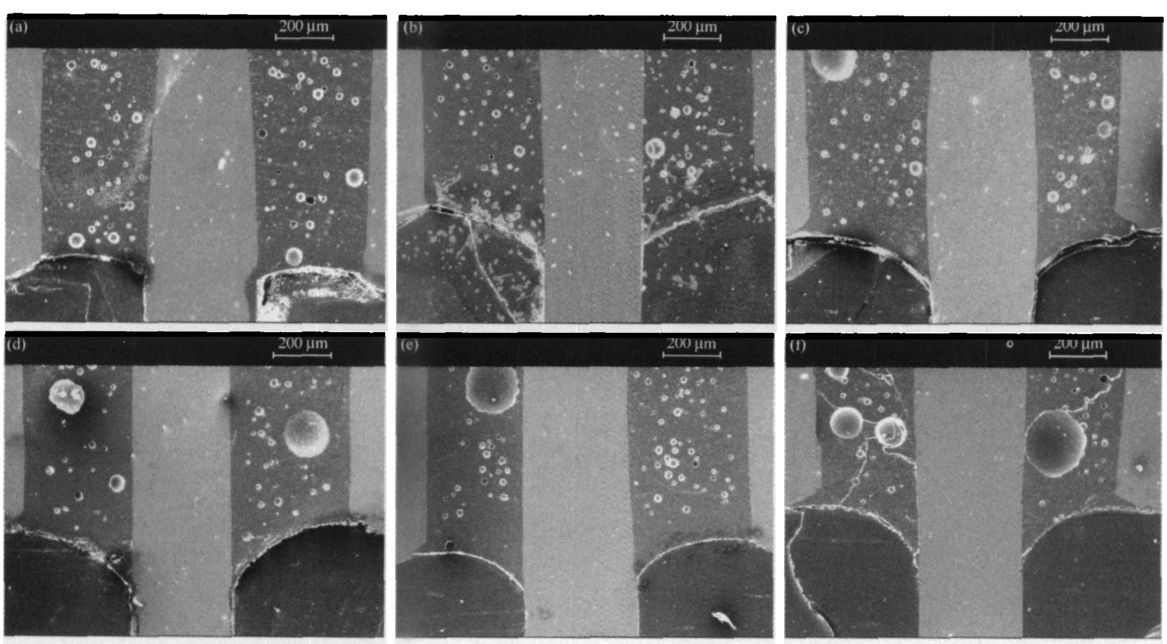

Fig. 1. Cross-sections of seals obtained by Kovar plates and pins first oxidized at 1000°C in N_2 with 20°C dew point for (a) 5 min, (b) 10 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min, then sealed with glass.

The relationship of oxide thickness with glass climbing height was linear as seen in Fig. 3. Because glass climbing height mainly reflected the wettability of glass to oxides, namely a thicker oxide, especially Fe_2O_3, was beneficial to the wettability of glass to oxide, thus promoting molten glass to climb along the pins.

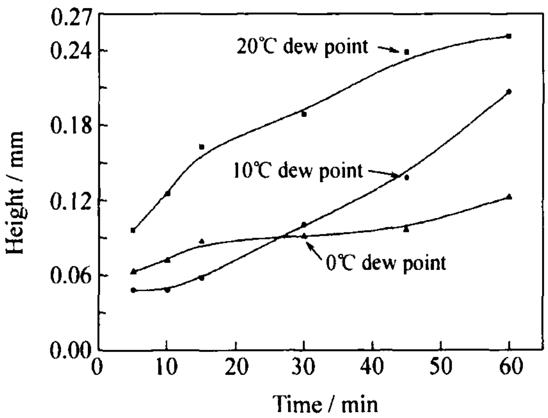

Fig. 2. Relationship between glass climbing height and oxidation time.

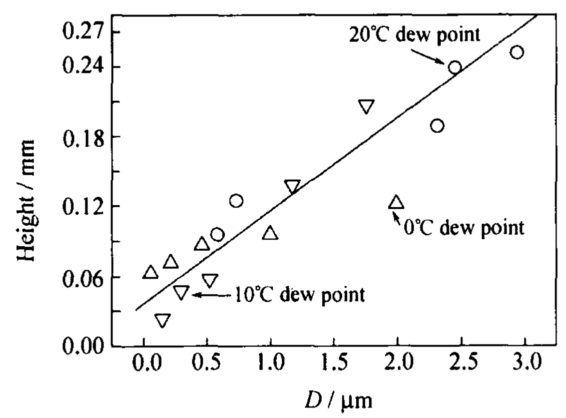

Fig. 3. Relationship between glass climbing height and oxide thickness.

3.3. Pattern of sealing interface

For the seals which had the thickest and thinnest oxide, the sealing interfaces were observed by SEM. And Fig. 4(a) shows the pattern of sealing interface which was obtained by Kovar alloy oxidized at 1000°C in N_2 with a dew point of 20°C for 60 min then sealed with glass, it clearly indicated that the surface of the pins was very rough when Kovar plates and pins were oxidized under the conditions, that is to say the surface of Kovar pins subjected to localized corrosion. Fig. 4(b) shows the pattern of sealing interface which was obtained by Kovar alloy oxidized at 1000°C in N_2 with a dew point of 0°C for 5 min then sealed with glass, which represented the thinnest oxide layer. It obviously showed that the surface of Kovar pins was smooth, namely uniform corrosion occurred.

3.4. Pull test of pins

Ten pins of every seal were pulled out of the glass bead using a WDS-5 microcomputer controlling electronic universal tester, and the pull force was measured. The results indicated that all the pull force exceeded 60 N, and some of them reached 90 N. These pull forces represent bond strength between glass and pins. The oxide thickness and oxidation time have large effect on the average pull force as shown in Figs. 5 and 6. Under the research conditions, the thinner the oxide layer, the lower the pull force, and the pull force increased with oxide thickness or oxidation time, but did not increase when the oxide thickness reached 0.5-0.75 μm. So it is unnecessary to enhance bond strength by increasing oxide thickness.

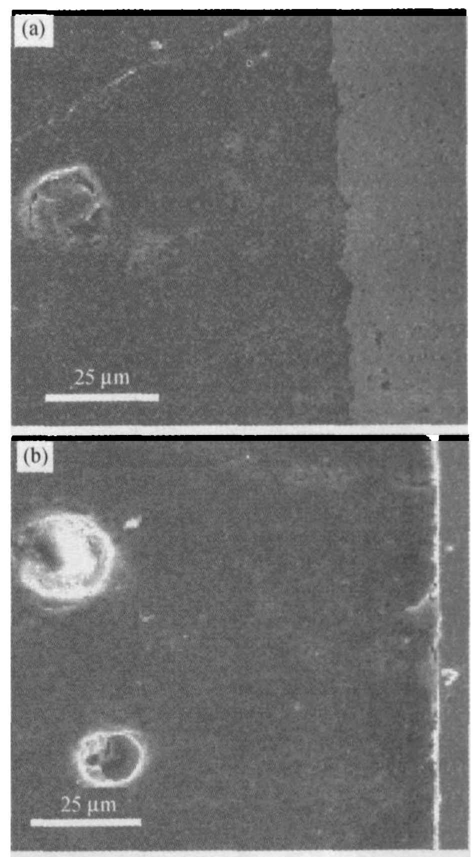

Fig. 4. Patterns of sealing interface which was obtained by Kovar alloy oxidized at 1000°C in N_2 with a dew point of 20°C for 60 min (a) and with a dew point of 0°C for 5 min (b), then sealed with glass.

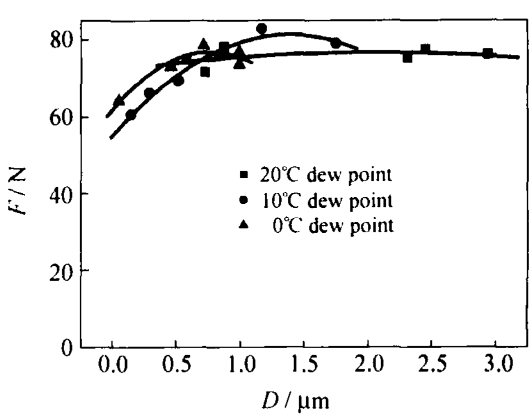

Fig. 5. Relationship between tensile force and oxide thickness.

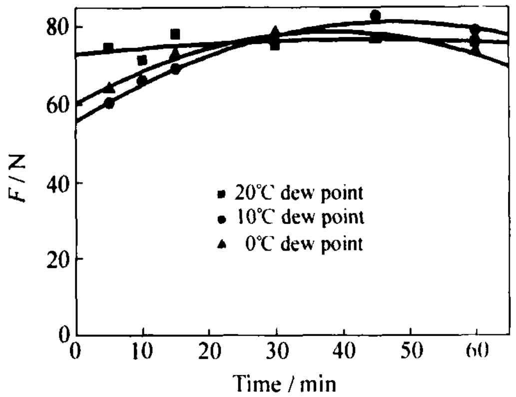

Fig. 6. Relationship between tensile force and oxidation time.

3.5. Surface pattern of pins pulled out from the glass bead

The surface of pins pulled out from the glass bead was observed by SEM. Fig. 7 shows their surface patterns with varying oxidation time in N_2 with 20°C dew point. The upper part of the pins was an original area bonded with glass insulator, and the middle of the pins is an original place of glass meniscus in Fig. 7.

It is obvious that the diameters of upper and lower pins are different, as seen in Figs. 7(a), (b) and (c), the upper pins bonded with the glass insulator distinctly became thinner, and formed sidestep at the meniscus. This indicates that the surface of the pins was subjected to corrosion action from molten glass in the sealing step when the oxide layer was thinner. But these corroded surfaces were very smooth, and they were uniform corrosion, and this was consistent with the observations of Fig. 4(b). As seen in Figs. 7(d)-(f), and (f), with increasing oxidation time, in other words, with increasing the oxide thickness and the quantity of Fe_2O_3, the diameters of upper and lower pins were almost the same, but the surfaces became rough, and were covered by numerous glass, and the corrosion type of the pins changed from uniform corrosion to localized corrosion. This was in accord with the pattern of Fig. 4(a). And similar rules were gained from the pins which were oxidized in N_2 with 10°C and 0°C dew points for different oxidation times. It is amazing that it exhibited the most serious uniform corrosion under the condition of the thinnest oxide when Kovar alloy was oxidized in N_2 with 0°C dew point for only 5 min (Fig. 8).

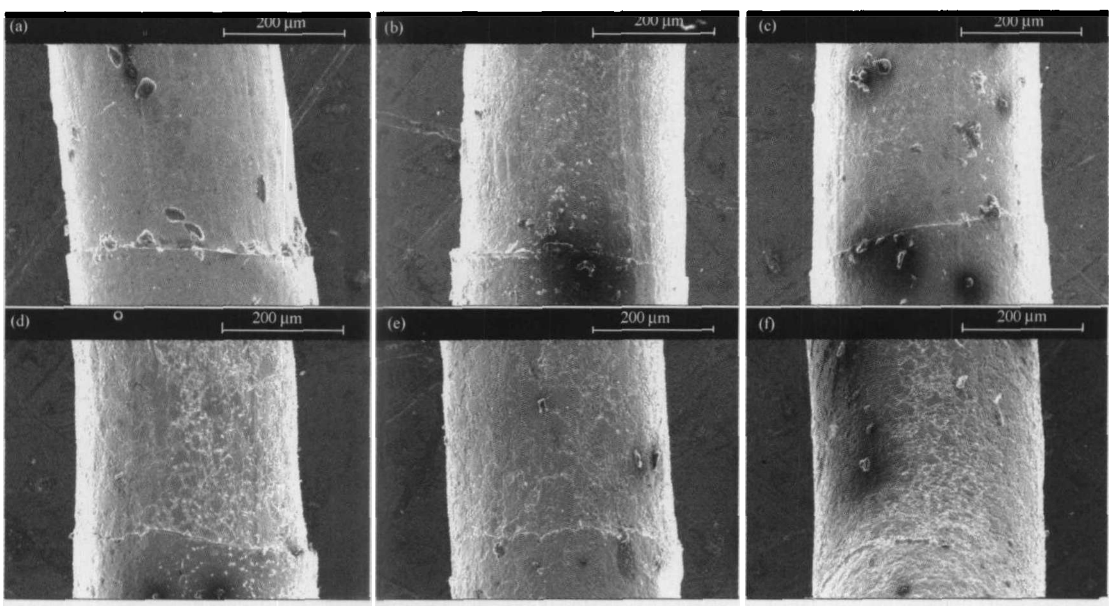

Fig. 7. Patterns of pulled pins oxidized in N_2 with a dew point of 20°C for different oxidation times: (a) 5 min; (b) 10 min; (c) 15 min; (d) 30 min; (e) 45 min; (f) 60 min.

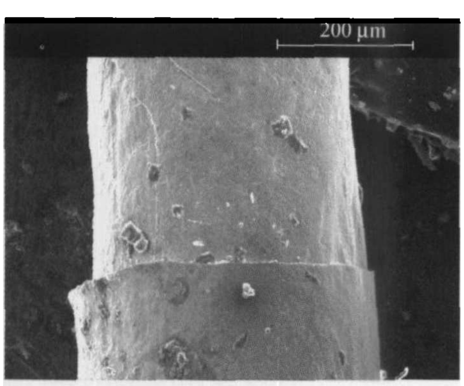

Fig. 8. Pattern of pulled pins oxidized in N_2 with a dew point of 0°C for 5 min.

Cracks were also found near the glass meniscus on the surface of pins. Fig. 9 shows an example in which Kovar pins were oxidized in N_2 with 10°C dew point for 15 min and 45 min, respectively. Their differences were that the pin surfaces were not covered by glass when the oxide was thinner (Fig. 9(a)), and the entire pin surface in the sealing zone and local pin surface above the meniscus were covered by glass when the oxide was thicker (Fig. 9(b)). They indicated that molten glass could lead to corrosion cracking of pins. And it is consistent with the previous analysis [10], which pointed out that a distinct decrease of the numbers of bend after sealing with glass should be attributed to the penetration of glass into the grain boundary of the pins near the meniscus, and then caused grain boundary embrittlement.

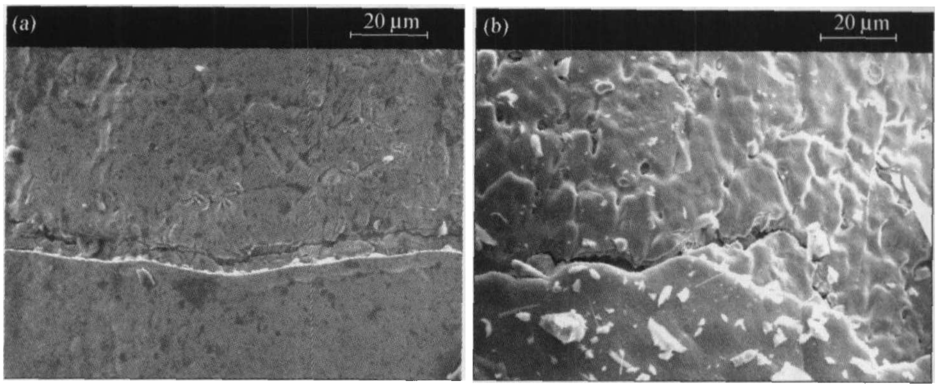

Fig. 9. Local patterns of the pins near the glass meniscus when oxidized in N_2 with a dew point of 10°C for (a) 15 min and (b) 45 min.

4. Conclusions

(1) The preoxidation of Kovar alloy would cause different gas bubbles' phenomenon in glass insulator after sealing, and the trend of gas bubbles was related to the type and quantity of oxides.

(2) Oxide thickness affected the climbing height of glass along the pins. The climbing height increased with oxidation time in N_2 with the same dew point, and also increased with dew point in the same oxidation time.

(3) The thinner the oxide layer, the lower the pull force, and the pull force increased with oxide thickness or oxidation time, but the pull force did not increase further, when the thickness of oxides exceeded 0.5-0.75 μm.

(4) The surfaces of the pins were subjected to corrosion action by molten glass in the sealing step. Uniform corrosion mainly occurred in the case of thinner oxides and localized corrosion occurred in the case of thicker oxides.

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