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Sn-Pd-Ni ELECTROPLATING ON Bi_2Te_3-BASED THERMOELECTRIC ELEMENTS FOR DIRECT THERMOCOMPRESSION BONDING AND CREATION OF A RELIABLE BONDING INTERFACE

The Sn-Ag-Cu-based solder paste screen-printing method has primarily been used to fabricate Bi_2Te_3-based thermoelectric (TE) modules, as Sn-based solder alloys have a low melting temperature (approximately 220°C) and good wettability with Cu electrodes. However, this process may result in uneven solder thickness when the printing pressure is not constant. Therefore, we suggested a novel direct-bonding method between the Bi_2Te_3-based TE elements and the Cu electrode by electroplating a 100 μm Sn/ 1.3 μm Pd/ 3.5 μm Ni bonding layer onto the Bi_2Te_3-based TE elements. It was determined that there is a problem with the amount of precipitation and composition depending on the pH change, and that the results may vary depending on the composition of Pd. Thus, double plating layers were formed, Ni/Pd, which were widely commercialized. The Sn/Pd/Ni electroplating was highly reliable, resulting in a bonding strength of 8 MPa between the thermoelectric and Cu electrode components, while the Pd and Ni electroplated layer acted as a diffusion barrier between the Sn layer and the Bi_2Te_3 TE. This process of electroplating Sn/Pd/Ni onto the Bi_2Te_3 TE elements presents a novel method for the fabrication of TE modules without using the conventional Sn-alloy-paste screen-printing method.

Keywords: Tin Electroplating, Thermoelectric Module, Thermocompression Bonding, Bi2Te3, Direct Bonding

1. Introduction

Studies on thermoelectric (TE) technology have attracted abundant attention recently in the aviation, space, computer, and automotive industries as the interest in eco-friendly non-carbon emissions has increased. In particular, Bi_2Te_3-based TE modules that exhibit excellent TE performance at relatively low temperatures of 100°C-200°C are the most widely studied. The structure of the TE module comprises several tens to hundreds of n-type and p-type TE devices joined in a series on top of a Cu electrode formed on a ceramic substrate. Therefore, a defect in one joint can affect the performance of the entire TE module [1-9].

In general, Bi_2Te_3-based TE modules are manufactured by applying hot air to the TE device and the Cu electrode for soldering after screen-printing a Sn-3%Ag-0.5%Cu-based solder paste uniformly on the Cu electrode of a ceramic substrate [10-13]. However, if the solder paste is not evenly distributed on the Cu electrode, the thickness of the solder paste layer becomes non-uniform, which can lead to defects in the interface of the TE device during the screen-printing process [12-13].

Therefore, to address this problem, we devised a method for bonding TE devices directly onto Cu electrodes with no screen-printing. To suppress the formation of brittle Sn-Te-based intermetallic compounds, electroplating was applied to form a Pd-Ni diffusion barrier layer on the Bi_2Te_3-type TE device with subsequent electroplating of a Sn layer ~100 μm in thickness. The effect of the plating layer on the bond strength of the Bi_2Te_3-based TE device was investigated by measuring the bond strength of the TE modules manufactured by using this plating method. To alleviate the low solder wettability of the Ni-plated layer commonly used as the diffusion barrier layer, a Pd-plated layer was formed on the existing Ni-plated layer to enhance the bond strength. In addition, the factors that change the bond strength according to the type of plating layer applied were studied by analyzing the interface of the manufactured TE module junction and by evaluating the solder spreading rate and wettability.

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2. Experimental

Commercially available n-type ($Bi_2Te_{2.7}Se_{0.3}$) Bi-Te-based TE powders were mixed and sintered by spark plasma sintering in a Ø28 mm graphite mold at 350°C under pressure of 50 MPa. The fabricated TE sintered body was cut into a 3-mm-thick disk using electric discharge machining. The surface of the disk was roughened by sand-blasting #220 grit alumina powders onto the surface of the sintered body. The surface of the sand-blasted TE disk was cleaned by ultrasonic degreasing for 3 min in acetone and for 1 min in a NaOH solution at room temperature. During Ni plating of the Bi-Te-based TE disk, a Ni plating layer 3.5 µm in thickness was formed by electroplating using a solution of 300 g/L $NiSO_4$, 60 g/L $NiCl_2$, and 45 g/L H_3BO_3 at 50°C for 12.5 min at 2 ASD. The 1.3-µm Pd plating layer was formed by electroplating with a commercially available Pd plating solution (TP600, YoungIn Plachem Co., Ltd., Korea) at 50°C for 15 min at 0.5 ASD. A Sn plating layer of ~100 µm was then formed by electroplating with a commercial Sn plating solution at 2 ASD at 25°C for 4 h. The Sn-Pd-Ni electroplated TE disk was cut into cubes of 3 mm × 3 mm × 3 mm by using a wire cutting method. The TE module was fabricated using the thermocompression bonding method by treatment at 300°C on a hotplate for 20 min at a pressure of 15.6 kPa after applying the blocks to a Cu electrode on the alumina ceramics with flux.

The bond strength of the fabricated TE modules was analyzed by measuring the maximum shear load at breaking using a ball-shear tester (XYZTEC, Condor, Netherlands). The bond strength measurement was repeated 10 times for the TE modules fabricated under a given condition, and the average value was plotted on a graph. The fracture surface was further observed using a scanning electron microscope (SU8220, Hitachi, Japan) after measuring the bond strength. Elemental analysis of the bonding interface between the TE device and the solder was also performed using a field emission electron probe microanalyzer (FE-EPMA, JXA8530F, JEOL, Japan). In addition, to compare the solder wettability of the surface of the respective plated TE disks, a solder ball 0.76 mm in diameter was heated on a hot plate at 270°C for 90 s after applying flux. The solder spreading rate (%) was calculated by measuring the height of the solder ball in micrometers before and after soldering. A total of eight solder balls were used, and the average value was plotted in the graph.

3. Results and discussion

Figure 1 shows the effect of the plating layer on the bond strength of the Bi-Te-based TE modules before and after heat treatment. The average bond strength of the TE devices subjected to only Sn plating and that subjected to Sn-Pd-Ni electroplating differed 4.8-fold when measured at 2.25 MPa and 10.65 MPa, respectively. In addition, the bond strength increased about fourfold for the TE device treated with only Sn-Ni plating. This indicates that the Ni layer acts as a diffusion barrier layer for the Bi-Te-based TE device, resulting in a significant increase in the bond strength. The bond strengths of the Sn–Ni-plated and Sn-Pd-Ni-electroplated devices after heat treatment at 200°C for 200 h did not differ significantly from those of the devices prior to heat treatment. Therefore, it is inferred that the Sn-Pd-Ni electroplating layer is highly effective in significantly improving the bond strength between the Bi–Te-based TE device and the Cu electrode of the alumina substrate. In addition, the bond strength remained constant after heat treatment.

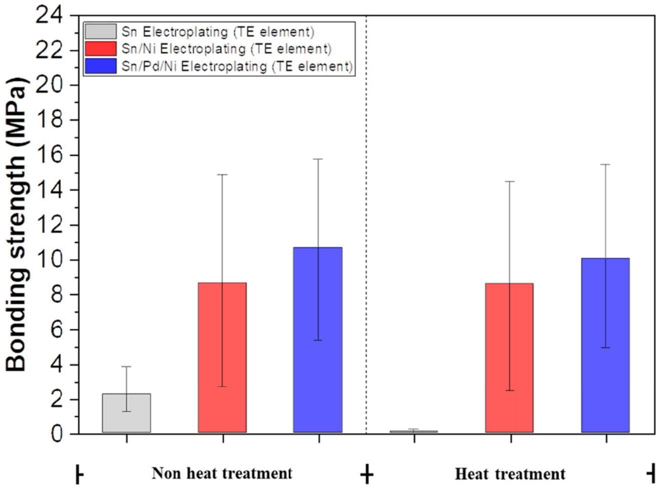
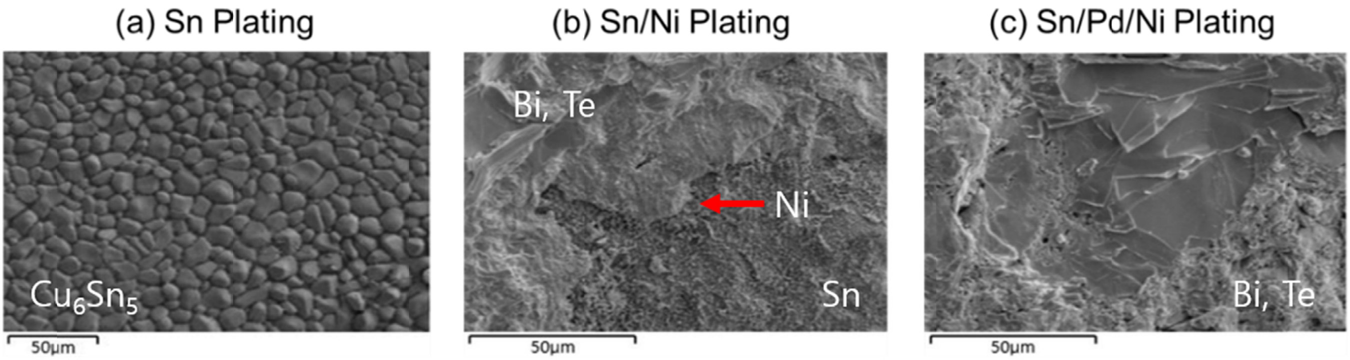


Fig. 1. Effect of the plating layer type on the bond strength of the Bi-Te-based TE modules before and after heat treatment

Figure 2 shows the results of scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) analysis of the fracture surface after measuring the bond strength of the TE modules with Sn plating, Sn-Ni plating, and Sn-Pd-Ni plating on the TE device. In the case of the TE device treated with only Sn plating (Fig. 2a, d), mainly Sn and Cu were detected; thus, it is confirmed that a fracture occurred between the plating layers. In the case of Sn-Ni plating [(b), (d)], Ni and Sn were detected in addition to the main components (Bi and Te) of the TE device, indicating that partial fractures occurred in the Ni plating layer and the TE device, respectively. In the case of Sn-Pd-Ni plating (Fig. 2c, f), only Bi and Te were detected in the components of the TE device, indicating that fracturing occurred in the TE device. It is inferred that the fracture occurred inside the TE materials rather than at the joint interface because the shear strength of the module joint is higher than that of the TE materials [9-17]. Therefore, the Sn-Pd-Ni electroplating was most effective for improving the bond strength between the Bi–Te-based TE device and the Cu electrode.

Figure 3 shows the FE-EPMA data for the bonding interface of the TE module subjected to Sn-Pd-Ni electroplating. A Ni diffusion barrier was formed uniformly at the bonding interface of the TE module with no interface defects such as pores. The formation of intermetallic compounds between Sn and Te was suppressed because the diffusion of Bi and Te was negligible under the Ni plating layer. Moreover, the Pd in the electroplated Pd layer rapidly diffused into the Sn layer to form intermetallic



(d) Sn Plating SEM-EDS spectrum (e) Sn/Ni Plating SEM-EDS spectrum (f) Sn/Pd/Ni Plating SEM-EDS spectrum

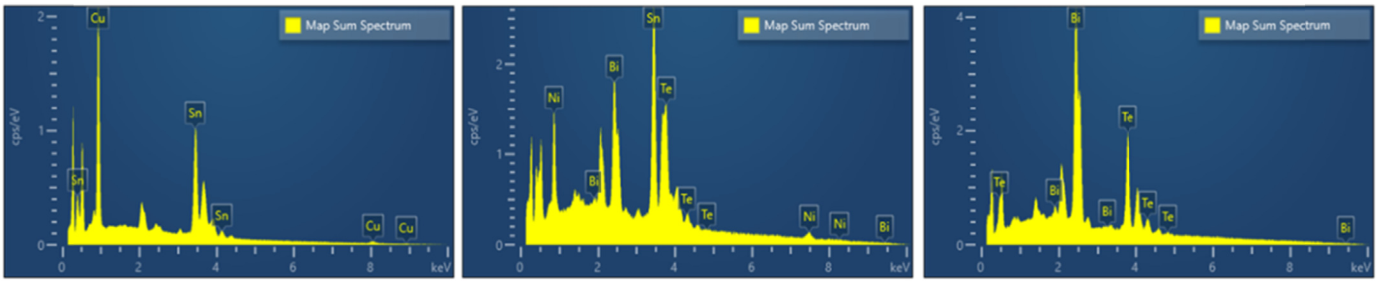


Fig. 2. SEM-EDS analysis of the fracture surface after measuring the bond strength. Sn plating [SEM image (a), EDS image (d)], Sn/Ni plating [SEM image (b), EDS image (e)], and Sn/Pd/Ni plating [SEM image (c), EDS image (f)]

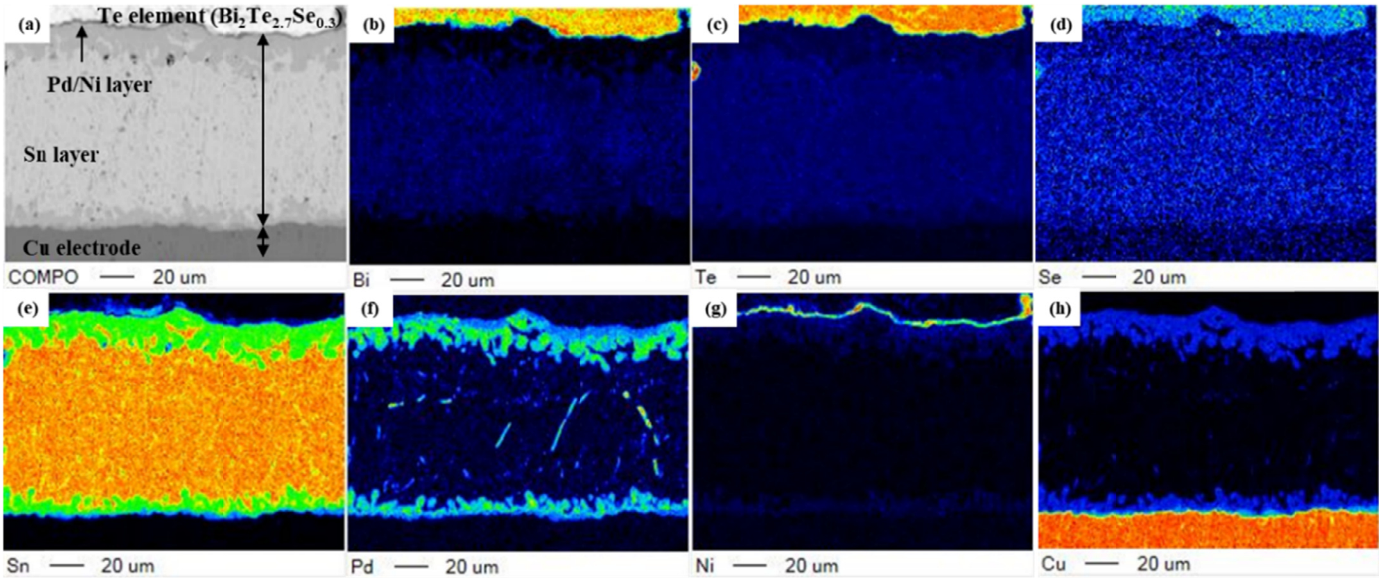


Fig. 3. FE-EPMA analysis of the bond interface of the TE module subjected to Sn-Pd-Ni electroplating [BSE image (a), (b) Bi, (c) Te, (d) Se, (e) Sn, (f) Pd, (g) Ni, and (h) Cu]

compounds with the Sn. In these intermetallic compounds Pd, Sn, and Cu were present. Pd diffuses rapidly to reach the Cu electrode board, and Cu reaches the Ni barrier layer. Pd, Cu, which reached the both sides, formed a compound between Sn and metal. Thus, it is inferred that the electroplated Pd layer not only serves as a diffusion barrier layer that prevents diffusion between the TE device and the solder but also forms Pd-Sn-Cu intermetallic compounds in the solder owing to rapid diffusion into the solder layer [11-17].

Figure 4 shows the effect of the plating layer on the solder spreading rate and wetting angle. The solder spreading rate of the Pd-Ni plating (Fig. 4b) increased about 54% compared with that of the Ni plating (Fig. 4a), and the wetting angle decreased 120°. A higher solder spreading rate and smaller wetting angle enable faster interdiffusion of TE device and the molten solder and of the electrode and the molten solder. The average solder spreading rate of the Ni-plated TE device was 7.9%, which is very low. However, the average solder spreading rate increased to 62.5% when the Pd plating layer was formed on the Ni plating layer. Therefore, these results reveal that the Pd-Ni-plated TE device had the highest bond strength owing to the formation of a thicker diffusion layer with the solder layer [11-15].

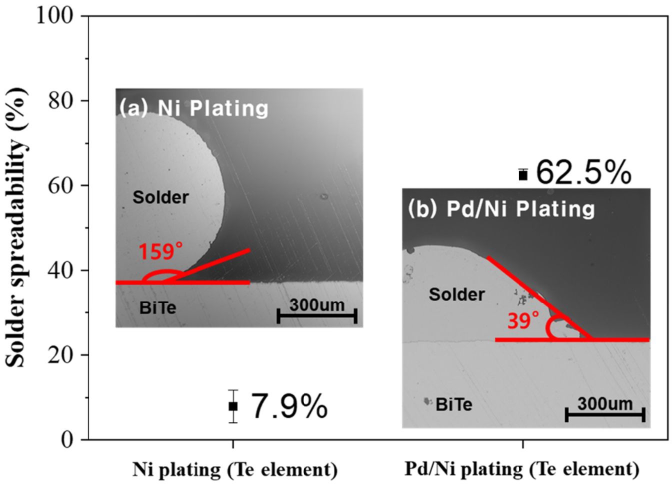


Fig. 4. Effect of the plating layer type on the solder spreading rate and the contact (wetting) angle – [(a) Ni plating wetting angle and (b) Pd/Ni plating wetting angle]

4. Conclusions

In this study, a TE module thermocompression direct bonding process was developed by forming a Sn-plated layer on a TE device without using the conventional screen-printing method. The effect of the type of plating layer on the bond strength of the fabricated Bi_2Te_3-based TE module was also investigated. The average bond strength of the TE device with Sn plating alone and that with Sn-Pd-Ni electroplating was 2.25 MPa and 10.65 MPa, respectively, representing a 4.8-fold increase. Only Bi and Te were detected in the fractured part of the TE module with Sn-Pd-Ni plating, suggesting that the fracture occurred in the TE device. It is inferred that the fracture occurred inside the TE materials rather than at the joint interface. According to the analysis of the bonding interface by FE-EPMA, the electroplated Pd layer not only acted as a diffusion barrier layer to prevent diffusion between the TE device and the solder but also formed Pd-Sn-Cu intermetallic compounds in the solder owing to rapid diffusion into the solder layer. The Pd-Ni-plated TE device showed the highest bond strength because the diffusion layer with the solder layer was thicker.

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