

SUBIN KIM<sup>1</sup>, SUNG HWA BAE<sup>2\*</sup>, INJOON SON<sup>1\*</sup>**EFFECT OF THE ENEPIG PROCESS ON THE BONDING STRENGTH OF BiTe-BASED THERMOELECTRIC ELEMENTS**

To improve the mechanical performance of BiTe-based thermoelectric modules, this study applies anti-diffusion layers that inhibit the generation of metal intercompounds and an electroless nickel/electrode palladium/mission gold (ENEPIG) plating layers to ensure a stable bonding interface. If a plated layer is formed only on BiTe-based thermoelectric, the diffusion of Cu in electrode substrates produces an intermetallic compound. Therefore, the ENEPIG process was applied on the Cu electrode substrate. The bonding strength highly increased from approximately 10.4 to 16.4 MPa when ENEPIG plating was conducted to the BiTe-based thermoelectric element. When ENEPIG plating was performed to both the BiTe-based thermoelectric element and the Cu electrode substrate, the bonding strength showed the highest value of approximately 17.6 MPa, suggesting that the ENEPIG process is effective in ensuring a highly reliable bonding interface of the BiTe-based thermoelectric module.

*Keywords:* thermoelectric, ENEPIG, bonding strength, BiTe, plating

**1. Introduction**

Research on the thermoelectric technology is gaining more attention with the recent increase in the demand for carbon-free environmentally friendly energy. In particular, thermoelectric modules composed of BiTe-system materials with a superior thermoelectric capability at low temperatures are most widely utilized in thermoelectric power generation to convert thermal energy to electric energy using the Seebeck effect [1-6]. These thermoelectric modules have n- and p-type thermoelements connected in a bonded structure on a Cu electrode on top of a ceramic board, such as alumina. All these thermoelements are connected in a series; hence, one poor joining affects the thermoelectric conversion capability of the whole module [1-6]. Meanwhile, a BiTe-system thermoelement and a Cu board are joined by a lead-free solder (Sn-Ag-Cu and Sn-Bi systems) with a melting point of ~220°C and a soldering process. If the diffusion barrier is not coated on the BiTe-system thermoelement and Cu electrode surface, brittle metallic compounds, such as the Sn-Te or Cu-Sn system, are formed on the bonding interface. The BiTe surface has a poor wettability with solder; hence, it forms defects, such as pores, on the bonding interface and consequentially results in a low bonding strength [7-10]. If an electroless Ni-P plating layer is coated on the BiTe-system thermoelement surface, the bonding strength is enhanced, but the wettability with the solder

is not significantly improved. To improve these shortcomings, the electroless nickel electroless palladium immersion gold (ENEPIG) surface treatment process that acts as a diffusion barrier and has superior wettability with lead-free solder was applied on the BiTe-system thermoelement and Cu electrode surface to improve the bonding strength [11-16].

To this end, ENEPIG plating was performed herein on a BiTe-system thermoelement and a Cu electrode substrate surface to inhibit the brittle intermetallic compound formation and obtain superior wettability with lead-free solder [11-16]. Furthermore, the bonding strength was compared with the existing electroless nickel (EN) process to investigate the effect of the ENEPIG on the bonding strength. The ENEPIG mechanism for improving the bonding strength was investigated through an interface analysis of the fracture surface and the connected part along with the measurement of the solder spread rate and the wet angle after measuring the bonding strength of the manufactured thermoelectric module.

**2. Experimental**

In this study, an n-type BiTe thermoelement ( $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ) was used for the experiments. The n-type BiTe powder was sintered in 30 mm diameter and 20 mm height through spark plasma

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sintering under the conditions of 360°C and 50 MPa. The sintered n-type BiTe was divided into a 3 mm disk by an electric spark machine. The BiTe surface roughness was subjected to a sand-blasting treatment with #220 alumina to roughen the surface and improve the adherence between the electrically discharged BiTe surface and the plating layer. The thermoelement was ultrasonically cleaned in acetone for 3 min and in a NaOH solution for 1 min before the plating. Pd catalyst (Atotech, Adhemax Activator SF, Germany) treatment was then conducted at 40°C for 3 min. Subsequently, pretreatment was performed with 5% HCl solution at 25°C for 1 min. Acidic cleansing of the Cu electrode substrate was conducted in K-MC (KPMTech Co. Ltd., K-MC, Korea) at 50°C for 5 min. Soft etching was then conducted in a potassium monopersulfate solution at 30°C for 90 s. Next, Pd catalyst treatment was performed in AC-1K (KPMTech Co. Ltd., AC-1K, Korea) at 25°C for 90 s. Electroless Ni plating was conducted using MPN-5 (KPMTech Co. Ltd., MPN-5, Korea) at 80°C for 20 min to form ~3 µm nickel plating layer. For electroless Pd plating, Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> (1 g/L), EDA (ethylenediamine), EDTA (ethylene-diamine-tetraacetic acid), C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>, and NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O solutions were prepared, and plating was performed at 55°C for 40 min to form ~0.18 µm palladium plating layer. Finally, for immersion Au plating, K[Au(CN)<sub>2</sub>] (1 g/L), K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, EDTA, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, and KH<sub>2</sub>PO<sub>4</sub> solutions were prepared, and plating was conducted at 85°C for 15 min to reach a plating layer thickness of ~0.07 µm. The plating layer thickness was measured using an X-ray plating thickness meter (XAN 250, Helmut Fischer, Germany). For the module manufacture, the plated BiTe disk was subjected to wire cutting to produce a 3\*3\*3 mm cube. To connect the thermoelectric module, a solder paste (Sn-3%Ag-0.5%Cu, SMIC Co., Ltd., M705, Korea) was spread on the Cu electrode substrate with ~0.18 mm thickness using the screen-printing method. Hot air treatment was then performed at 270°C for 10 min. The shear load at the fracture on the connected part was measured using a ball shear tester (XYZTEC, Condor, Netherlands) and converted to the bonding strength to determine the bonding strength of the manufactured thermoelectric module. For each surface treatment condition, the thermoelectric module bonding strengths were measured, and the average value was presented. Moreover, the bonding interface compositional analysis of the manufactured thermoelectric module was conducted using a field emission-electron probe microanalyzer (FE-EPMA, JEOL, JXA8530F, Japan). Finally, a solder ball with 0.76 mm diameter was placed on the plating layer to measure the solder spread rate and the wet angle of the plating layer. Heat treatment was subsequently performed at 270°C for 10 min to observe the change in spread solder height and the interface cross-section.

### 3. Results and discussion

Fig. 1 shows the change in the bonding strength of the thermoelectric module with different plating layer types. Subjecting both the BiTe thermoelement and the Cu electrode substrate to

the ENEPIG process produced the highest bonding strength of 17.5 MPa. On the contrary, the lowest value of 10.2 MPa was seen when both were subjected to the EN process. Moreover, the plating layer type on the BiTe thermoelement resulted in a more significant bonding strength change compared with that on the Cu electrode substrate. This shows that the ENEPIG surface treatment is an effective process for improving the bonding strength between the BiTe thermoelement and the Cu electrode [11-14].

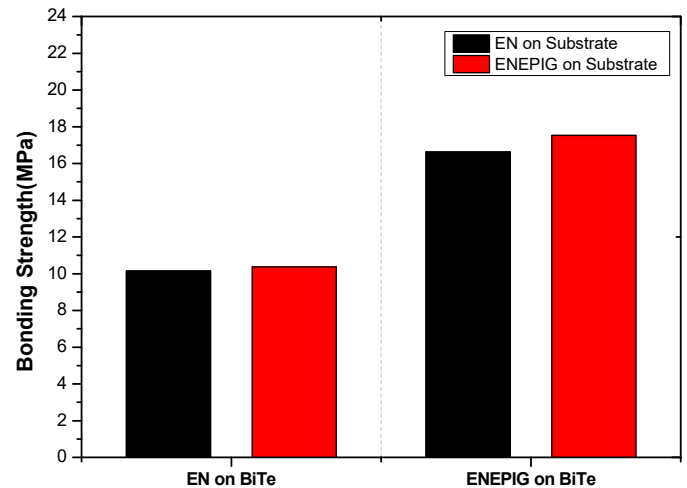


Fig. 1. Effect of the plating layers on the bonding strength of the Bi-Te thermoelectric elements

Fig. 2 depicts the FE-EPMA analysis results on the bonding interface of the thermoelectric module, where the ENEPIG process was conducted on the BiTe thermoelement and the Cu electrode substrate. Both the BiTe thermoelement and the Cu electrode board were uniformly joined without defects, such as pores and cracks, on the interface. The electroless Ni plating layer was present at the thermoelement and Cu electrode interface (e), while Sn was absent at the thermoelement (c) and electrode part (i); hence, the brittle Sn-Te and Cu-Sn system intermetallic compounds were not formed because of the ENEPIG layer. The ENEPIG plating layer acted as a diffusion barrier [11,12].

Fig. 3 presents the scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) results on the fracture surface after measuring the bonding strength of the thermoelectric module obtained after the ENEPIG process. Mostly Bi and Te were detected from the fractured part surface probably because the shear strength of the module connected part was higher than that of the thermoelectric material; the joint interface of the plating layer was not fractured; and the fracture occurred in the thermoelectric material [12-14]. The partial Ni detection indicated that a portion of the Ni and the BiTe thermoelement was separated during the fracture.

Fig. 4 illustrates the spread rate and the wetting angle of the solder ball (0.76 mm) on the EN and ENEPIG plating layers. The solder spreadability was calculated by measuring the difference in height before and after melting the solder ball in an environment of 270°C and 10 minute on the surface of the plating



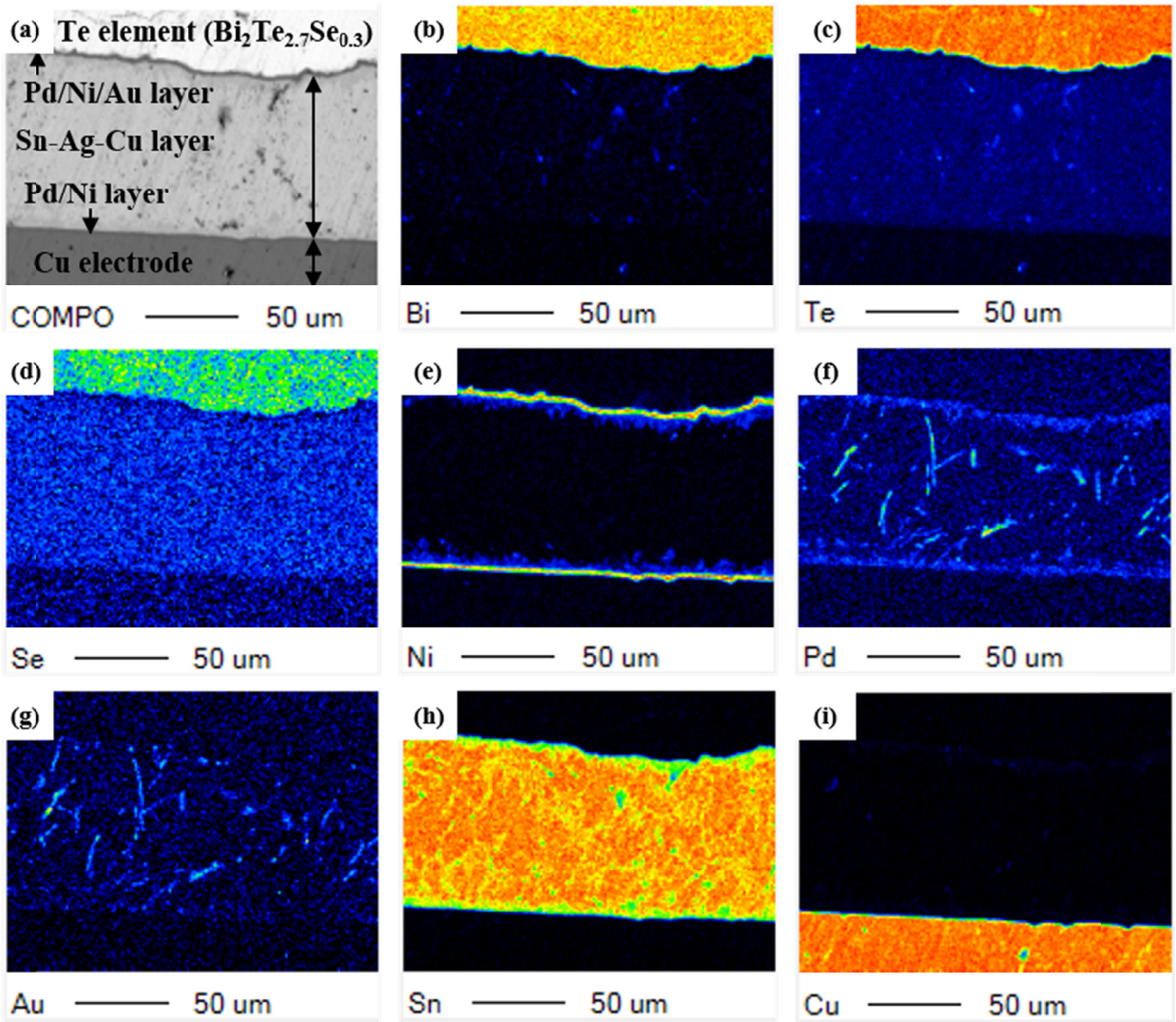


Fig. 2. Interface analysis results on the cross-section of the connected part of the n-BiTe and Cu electrode surfaces obtained after the ENEPIG process utilizing FE-EPMA

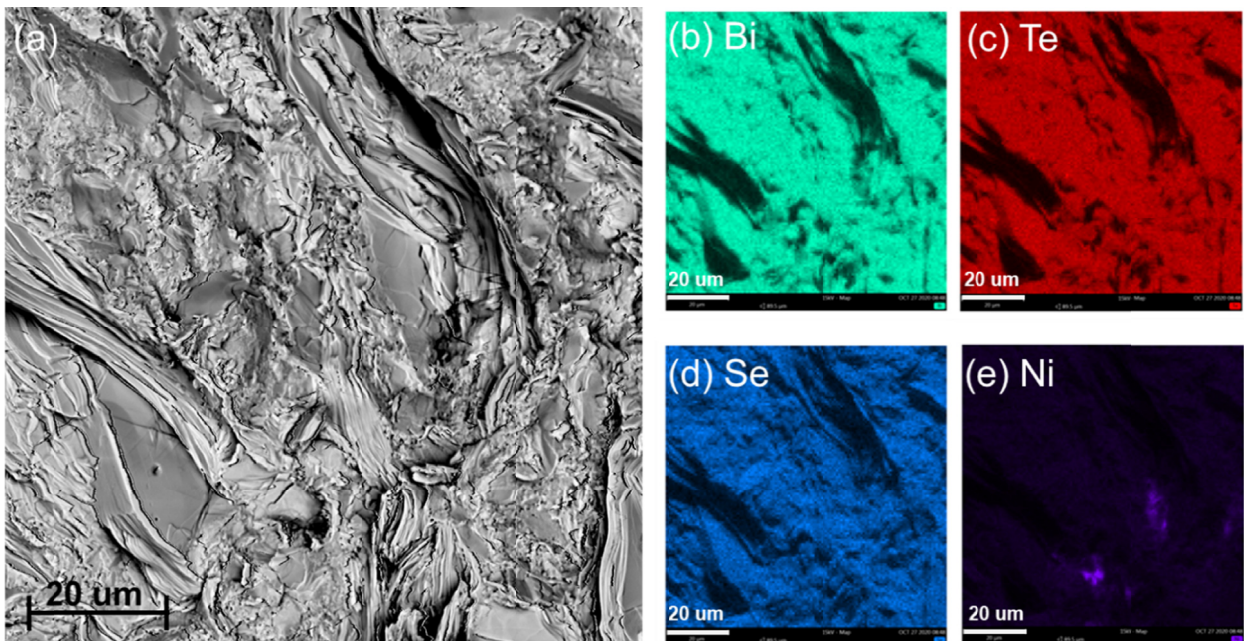


Fig. 3. SEM-EDS analysis on the thermoelectric module fracture part obtained after the ENEPIG process

layer. At a higher solder spread rate, the plating layer surface and the melting solder were interdiffused into each other at a fast rate [12]. The solder spread rates of the EN and ENEPIG plating layers were 26.3% and 75.7%, respectively, indicating that the spread rate of the latter was approximately 50% higher than that of the former. Moreover, the wetting angles of the EN and ENEPIG plating layers were  $140^\circ$  and  $41^\circ$ , respectively, demonstrating that the solder wettability was significantly improved by the ENEPIG treatment. Au in the ENEPIG plating layer is known to be the fastest element in the diffusion to the melting solder. The higher solder spread rate indicates that the diffusion layer with the solder layer is more thickly formed, while defects, such as pores, are not expected to be formed on the bonding interface with superior solder wettability [12]. Therefore, the solder wettability along with the bonding strength was expected to be improved when the ENEPIG surface treatment was conducted on the BiTe thermoelement and the Cu electrode surface.

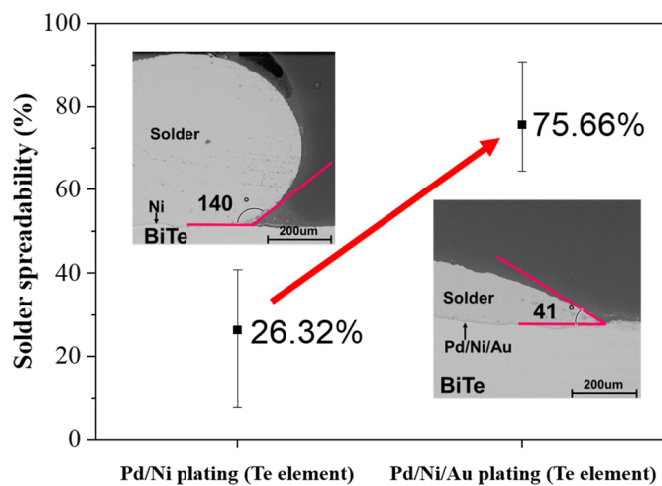


Fig. 4. Effect of the plating layers on the solder spreadability and wetting angle

#### 4. Conclusions

This study investigated the effect of the ENEPIG process on the bonding strength of the BiTe-system thermoelectric module. When the ENEPIG process was conducted on the BiTe thermoelement and the Cu electrode substrate, the bonding strength increased by 7.5 MPa compared with that when the EN process was performed. The Ni plating layer of the ENEPIG process acted as a diffusion barrier to suppress the formation of intermetallic compounds of chamois Sn-Te and Cu-metallic. The ENEPIG process improved joint strength in both Cu electrodes and BiTe, with plating layer types having a more significant impact on BiTe. Compared with the EN process, the ENEPIG process enhanced the solder spreadability and wettability, consequently resulting in superior bonding strength.

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