This study investigated the soldering and thermal aging reactions of Sn and Bi₂Te₃-based thermoelectric materials (p-type and n-type) with two diffusion barrier materials, Ni and Co. Unlike the conventional electroplating method, electroless deposition of Ni(P) or Co(P) is applied in this study. The microstructure evolution for various reaction cases were examined with different reaction times. For the Ni-P cases, the formed phases were very complex, especially in the n-type, including Ni₃Sn₄, Ni-Sn-P, NiTe, (Ni,Te)₃Sn₄, SnTe and BiTe. For the Co-P cases, the CoSn₄, Co-Sn-P and SnTe phases were formed. Furthermore, in the liquid-state reaction, the Ni-P layer severely peeled off from the interface when soldering for only 1 min. Additionally, in the Co-P cases, the Co-P layer was rapidly consumed to form the metastable CoSn₄ phase and Co-Sn-P, and massive spallation of the CoSn₄ phase occurred.

Thermoelectric (TE) devices consist of many pairs of p-type (Bi₁₋ₓSbₓTe₃₋ₓ) and n-type (Bi₁₋ₓTeₓSe₃₋ₓ) semiconductors, which are electrically connected with Cu plates by soldering. When TE substrates react with molten solders, intermetallic compounds (IMCs) form abnormally fast. Ni is frequently electroplated on TE substrates as a temporary diffusion barrier layer. However, Ni-P or Co-P layer undergoes abnormal fast consumption. Ni is frequently electroplated on TE substrates as a temporary diffusion barrier layer. When TE substrates are bonded to Cu plates, Ni-P or Co-P layers were rapidly consumed to form Ni₃Sn₄ and NiTe, respectively.

For the n-type case, another BiTe phase was produced adjacent to the TE substrate. We investigated a series of solid- and liquid-state interfacial reactions between pure Sn and Ni-P (or Co-P) deposited on Bi₂Te₃-based substrates. The reactions of Ni-P and Sn were much faster than the Ni-P cases. For the Sn-58Bi/Co-P/TE case, a layer-structured CoSn₄ was found and the SnTe was simultaneously formed. For the p-type case, NiTe was transformed into (Ni,Te)₃Sn₄ when Ni-P was depleted, and the SnTe and BiTe phase were formed. The IMCs massively spalled into the solders when the Co-P was completely consumed. The spalling did not occur.

For the solid/solid Sn/Co-P/TE reactions, the CoSn₄ was formed. The IMCs massively spalled into the solders when the Co-P was completely consumed. When the Co-P consumed completely, the SnTe and BiTe were then formed for the n-type case. For the Sn-58Bi/Co-P/TE case, a layer-structured CoSn₄ was found and the spalling did not occur.

Conclusions
- For the Ni-P cases, Ni₃Sn₄ and NiTe were the major formed phases in the initial solid-state reaction. Additionally, for the n-type case, NiTe was transformed into (Ni,Te)₃Sn₄ when Ni-P was depleted, and the SnTe and BiTe were simultaneously formed.
- For the solid/solid Sn/Co-P/TE reactions, the CoSn₄ was formed. When the Co-P consumed completely, the SnTe was rapidly formed and the BiTe was observed for n-type reactions. Further investigation on inhibiting the solder/TE reactions using the Co-P barrier layer is required for industrial applications.