www.czasopisma.pan.pl PAN www.journals.pan.pl
POLSKA AKADEMIA NAUK

Arch. Metall. Mater. **62** (2017), 2B, 1225-1229

DOI: 10.1515/amm-2017-0182

S.S. KIM*, I. SON*#, K.T. KIM**

EFFECT OF ELECTROLESS Ni–P PLATING ON THE BONDING STRENGTH OF Bi–Te-BASED THERMOELECTRIC MODULES

In the present study, electroless Ni–P plating was applied to Bi–Te-based thermoelectric materials as a barrier layer and the effect of the Ni–P plating on the bonding strength of the thermoelectric module was investigated. The bonding strength of the n- and p-type modules increased after being subjected to the electroless Ni–P plating treatment. In the case of the thermoelectric module that was not subjected to electroless Ni–P plating, Sn and Te were interdiffused and formed a brittle Sn–Te-based metallic compound. The shearing mostly occurred on the bonding interface where such an intermetallic compound was formed. On the other hands, it was found from the FE-EPMA analysis of the bonding interface of thermoelectric module subjected to electroless Ni-P plating that the electroless Ni-P plating acted as an anti-diffusion layer, preventing the interdiffusion of Sn and Te. Therefore, by forming such an anti-diffusion layer on the surface of the Bi–Te based thermoelectric element, the bonding strength of the thermoelectric module could be increased.

Keywords: Thermoelectric, Ni–P plating, Bonding strength, Bi–Te, Soldering

1. Introduction

Bi–Te-based thermoelectric modules show high performance at temperatures below 400 K, and they are most commonly used for converting thermal energy into electric energy and vice versa [1-5]. In thermoelectric modules, multiple n-type and p-type thermoelectric elements are electrically and serially joined on a copper electrode formed on a ceramic substrate. In the case of commercial thermoelectric modules, the number of thermoelectric elements can be as high as 280. Also, because the elements are all connected serially, the failure of a single joined thermoelectric element can affect the performance of the entire module.

For bonding of thermoelectric elements and the copper electrode, soldering is most commonly adopted, in which Sn alloys with low melting points are melted and added [6,7]. However, Sn, which is the major component of solder, and Te, a component of the thermoelectric elements, are known to form thick intermetallic compounds at approximately 520 K. This Sn–Te-based metallic compounds not only decrease the efficiency of the thermoelectric module but also decrease the strength of the thermoelectric module bonding due to its high brittleness [8,9].

In the present study, in order to prevent the interdiffusion between Sn and Te, an electroless Ni–P plating layer was applied to the surface of a Bi–Te-based thermoelectric element, thus forming an anti-diffusion layer. Moreover, by measuring the bonding strength of the manufactured thermoelectric module, the influence of the electroless Ni–P plating on the bonding strength of the Bi–Te-based thermoelectric element was investigated. In addition, through the surface and interface analysis of the manufactured thermoelectric module, the factors that increase the bonding strength of the thermoelectric module as a result of the electroless Ni–P plating are discussed.

2. Experimental

The bismuth (Bi) and tellurium (Te) powders were respectively added with small amounts of selenium (Se) and antimony (Sb). Using the same sintering conditions, disc-shaped n-type ($Bi_2Te_{2.7}Se_{0.3}$) and p-type ($Bi_{0.5}Sb_{1.5}Te_3$) thermoelectric elements with diameters of 25 mm and thicknesses of 3 mm were manufactured. Before conducting the electroless Ni–P plating, in order to enhance the adhesion between the Bi–Te-based thermoelectric element and the plating, the sand-blasting method was used in which alumina powders with average particle size of 70 μm were sprayed on the surface of the thermoelectric element, thus adjusting the surface roughness.

As pre-treatment of the electroless Ni–P plating, the thermoelectric element was immersed in a NaOH solution at room temperature for 60 s, for etching. Thereafter, the thermoelectric element was immersed in a commercial Pd-catalyzed solu-

* SCHOOL OF MATERIALS SCIENCE AND ENGINEERING, KYUNGPOOK NATIONAL UNIVERSITY, 80 DAEHAKRO, BUK-GU, DAEGU 702-701, KOREA
** POWDER & CERAMIC MATERIALS DIVISION, KOREA INSTITUTE OF MATERIALS SCIENCE, 797 CHANGWON-DAERO, SEONGSAN-GU, CHANGWON, GYEONGNAM 642-831, KOREA
# Corresponding author: ijson@knu.ac.kr

tion (Adhemax Activator SF, ATOTECH, Germany) at room temperature for 60 s to form Pd nuclei on the surface of the thermoelectric element. Then, the thermoelectric element was immersed in a commercial electroless Ni–P plating solution (YoungIn Plachem Co. Ltd, ENF, Korea) at 360 K for 20 min to form a Ni–P plating layer with a thickness of approximately 3 μm on the surface of the Bi–Te-based thermoelectric element.

The disc-shaped thermoelectric element formed with electroless Ni–P plating was cut into 3 mm×3 mm×3 mm squares using the wire-cutting method to manufacture the thermoelectric element blocks. To manufacture the thermoelectric module, the blocks were bonded onto a copper electrode formed on an alumina substrate at 533 K for 6 min by using a Sn–3.5Ag–0.5Cu-based soldering paste. The bonding strength of the thermoelectric module was measured by a Ball shear tester (Dage 4000, Nordson Corporation, USA). Regarding the thermoelectric module manufactured within the same condition, the bonding strength was measured five times in total and the values were averaged, as shown in the graphs. Also, by using field emission scanning electron microscopy (FE-SEM, SU8220, Hitachi, Japan) and field emission electron probe micro-analyzer (FE-EPMA, JXA8530F, JEOL, Japan), the interface of the bond and the sheared surface of the thermoelectric module were observed.

3. Results and discussion

Figure 1 shows the influence of the electroless Ni–P plating on the bonding strength of the Bi–Te-based thermoelectric modules. The average bonding strength of the n-type and p-type thermoelectric modules that were not subjected to electroless Ni–P plating were respectively 4.96 MPa and 6.42 MPa. However, the bonding strength of the thermoelectric modules after the electroless Ni–P plating were respectively 11.10 MPa and 12.62 MPa, indicating a significant increase. In other words, by the electroless Ni–P plating, the bonding strength of thermoelectric modules increased more than doubled. Considering that the bonding strength of both the n-type and p-type thermoelectric modules increased, the electroless Ni–P plating can be deemed as a highly efficient means for increasing the bonding strength of Bi–Te-based thermoelectric modules.

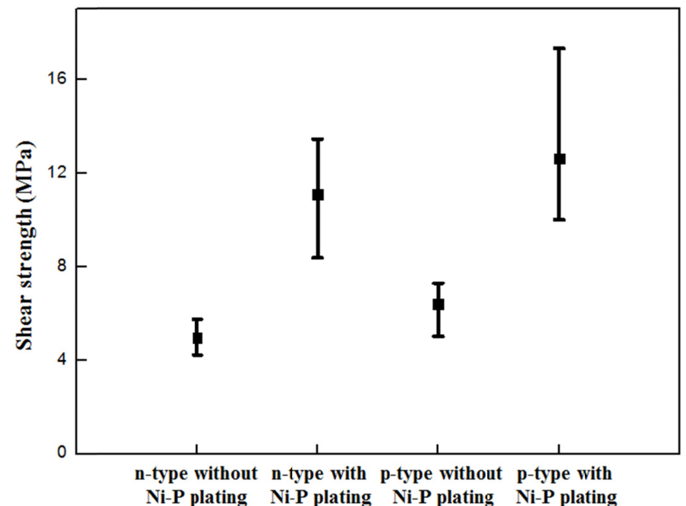

Fig. 1. Influence of electroless Ni–P plating on the bonding strength of the Bi–Te-based thermoelectric modules

Figure 2 shows the digital microscopic image and surface SEM image of the thermoelectric element block cut by the wire-cutting method after the electroless Ni–P plating. Because the bonding between the thermoelectric element and the electroless Ni–P plating layer was excellent, the plating was not exfoliated, even after the wire cutting (Fig. 2a). Moreover, during the SEM observation on the surface of the plating (Fig. 2b), the electroless Ni–P plating layer did not form defects such as pores on the surface of the thermoelectric element. Therefore, it can be inferred that the electroless Ni–P plating can be suitably adapted as an anti-diffusion layer of Bi–Te-based thermoelectric elements.

The bonding interface between the n-type thermoelectric module not subjected to electroless Ni–P plating and the solder was observed in cross section through elements analysis using FE-EPMA. The results are shown in Figure 3. In the SEM image (Fig. 3a), it can be seen that the thermoelectric element and the Sn–Ag–Cu-based solder are well bonded, without any interfacial defects such as pores or cracks. However, at the bonding interface, considering that both Te (Fig. 3c) and Sn (Fig. 3d) are almost equally distributed, it can be inferred that during the soldering, Sn, which is the major component of the solder, formed Sn–Te-based metallic compound through interdiffusion

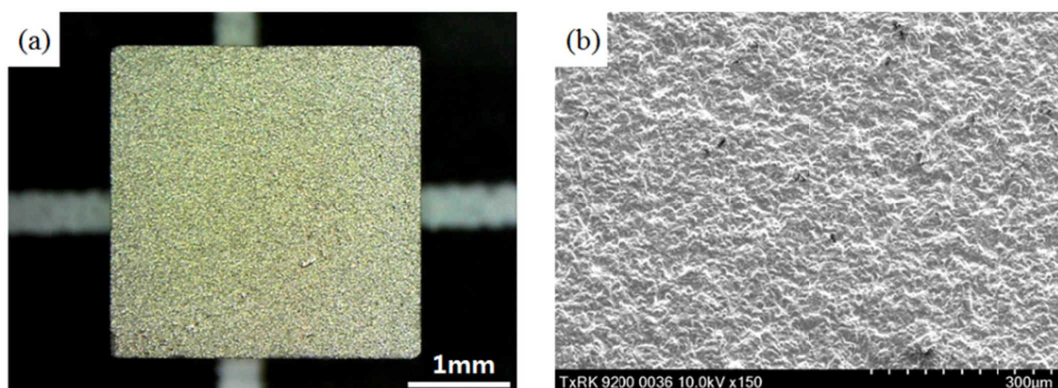

Fig. 2. (a) The digital microscopic image of thermoelectric element block after electroless Ni–P plating and (b) SEM image of its surface

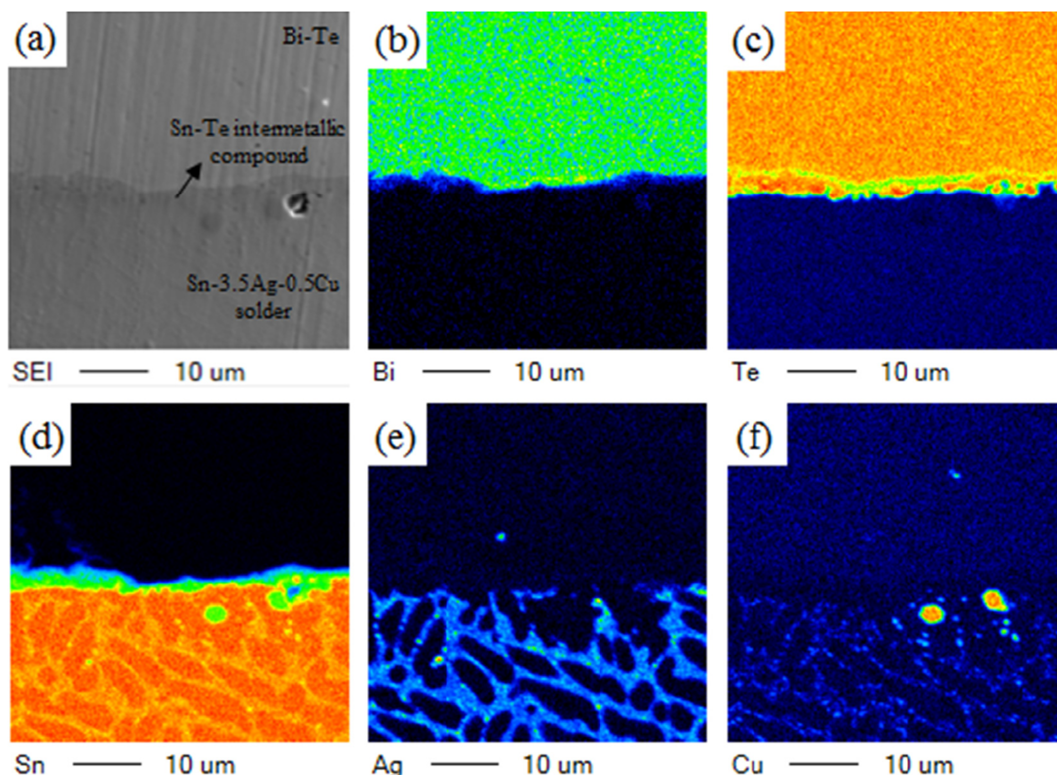

Fig. 3. FE-EPMA analysis of bonding interface of n-type thermoelectric module not subjected to electroless Ni–P plating; (a) SEM image, (b) Bi, (c) Te, (d) Sn, (e) Ag, (f) Cu

with the Te of the thermoelectric element. Because the Sn–Te-based metallic compound is brittle, this is expected to negatively influence the bonding strength. The same result was obtained from the FE-EPMA observation of the bonding interface of the p-type thermoelectric module.

Figure 4 shows the FE-EPMA analysis results of the bonding interface of the n-type thermoelectric module subjected to the electroless Ni–P plating. Considering that Ni (Fig. 4b) and P (Fig. 4c) were simultaneously detected from the bonding interface between the thermoelectric element and the solder, it can be inferred that the electroless Ni–P plating layer was formed on the surface of the bonding interface by a predetermined thickness. Meanwhile, Bi (Fig. 4d) and Te (Fig. 4e) were hardly detected from the solder bonding below the Ni–P plating layer. Also, con-

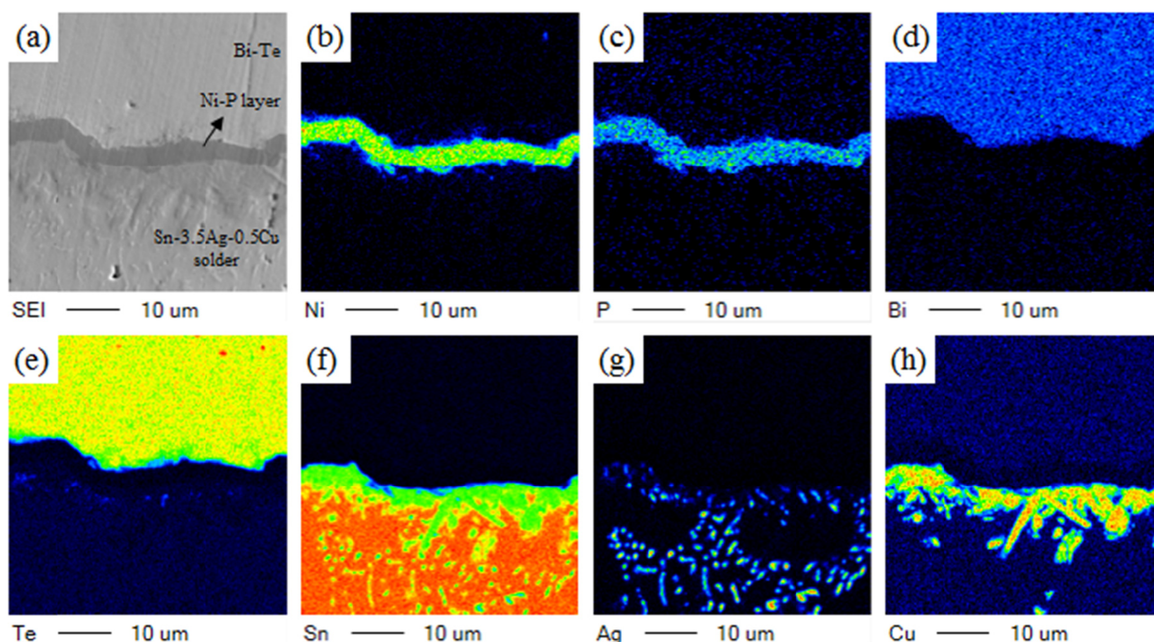

Fig. 4. FE-EPMA analysis of bonding interface of n-type thermoelectric module subjected to electroless Ni-P plating; (a) SEM image, (b) Ni, (c) P, (d) Bi, (e) Te, (f) Sn, (g) Ag, (h) Cu

sidering that Sn (Fig. 4f), Ag (Fig. 4g), and Cu (Fig. 4h), which are components of solder, only existed below the Ni–P plating layer, it can be inferred that the electroless Ni–P plating layer acted as an anti-diffusion layer, preventing the interdiffusion of both the thermoelectric element and solder. The same result was obtained from the FE-EPMA observation of the bonding interface of the p-type thermoelectric module.

The sheared surface of the thermoelectric module that was not subjected to the electroless Ni–P plating was observed after the bonding strength test, and the results are shown in Figure 5. On the surface of the sheared thermoelectric module, Sn (Fig. 5a) and Te (Fig. 5b) were observed at almost the same part. In the case in which electroless Ni–P plating was not conducted, Sn and Te were interdiffused to form a brittle metallic compound (Fig. 3), and so the shearing of the thermoelectric element mainly occurred at the bonding interface where the Sn–Te-based metallic compound was formed.

Figure 6 shows the sheared surface of the thermoelectric module subjected to electroless Ni–P plating after the bonding strength test. The sheared surface of the thermoelectric module shows a light-gray region, located on the left side of the sheared surface, in comparison to the thermoelectric module without the Ni–P plating. Inside the light-gray region, only Bi (Fig 6b) and Te (Fig. 6c) were present. The height of the thermoelectric element was also lower than on the right side, where Ni (Fig. 6d) was present. Therefore, this part is assumed to be the part where the thermoelectric element was sheared.

In the case of the thermoelectric module that was not subjected to electroless Ni–P plating, a Sn–Te-based metallic compound was formed by the interdiffusion of Sn and Te on the bonding interface (Fig. 3). Shearing also occurred mostly on the same bonding interface, where the brittle metallic compound was formed (Fig. 5). By conducting electroless Ni–P plating on the surface of the thermoelectric element, the bonding strength of the thermoelectric module increased more than doubled (Fig. 1). The electroless Ni–P plating efficiently acted as an anti-diffusion layer, preventing the interdiffusion of the thermoelectric element and the solder (Fig. 4). Therefore, by forming a uniform electroless Ni–P plating layer on the surface of a Bi–Te-based thermoelectric element, the interdiffusion between Sn and Te was prevented, thus enhancing the bonding strength by suppressing the formation of a brittle metallic compound.

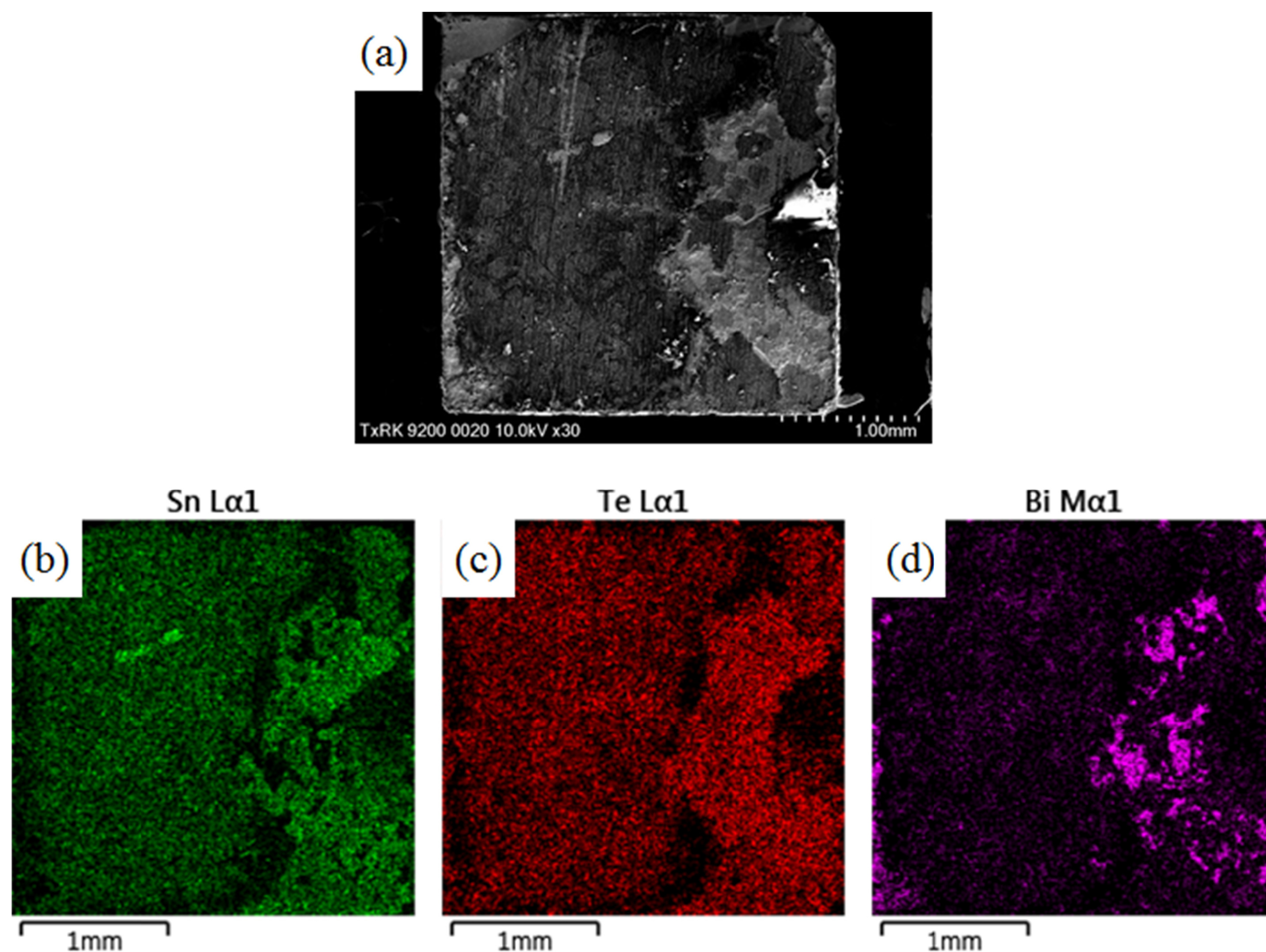

Fig. 5. FE-SEM analysis of sheared surface of n-type thermoelectric module not subjected to electroless Ni–P plating after bonding strength test; (a) SEM image, (b) Sn, (c) Te, (d) Bi

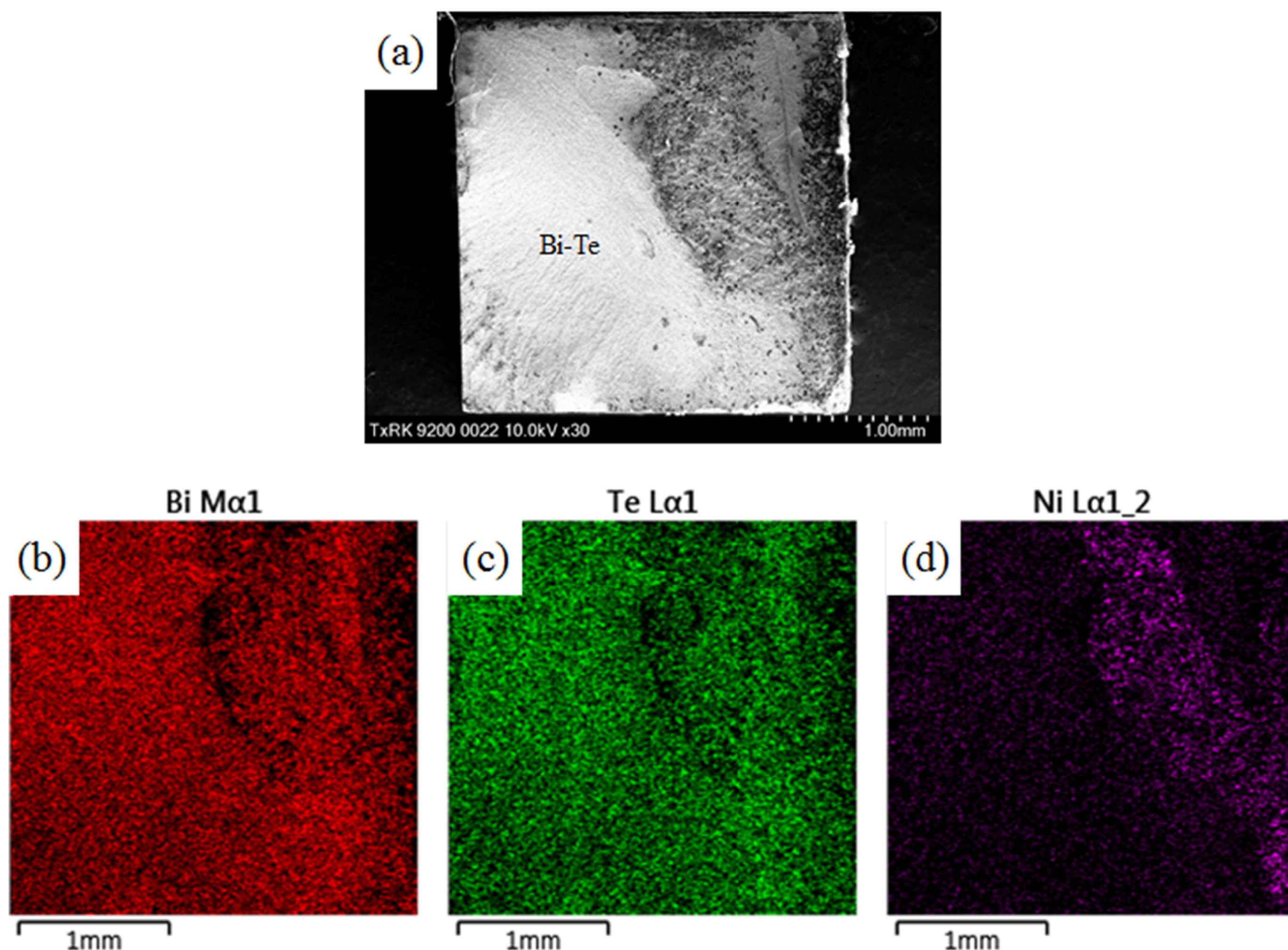

Fig. 6. FE-SEM analysis of sheared surface of n-type thermoelectric module subjected to electroless Ni–P plating after bonding strength test; (a) SEM image, (b) Bi, (c) Te, (d) Ni

4. Conclusions

In the present study, the influence of electroless Ni–P plating on the bonding strength of a Bi–Te-based thermoelectric module was investigated. By performing the electroless Ni–P plating, the bonding strength of both the n-type, and p-type thermoelectric modules increased more than doubled. On the bonding interface of the thermoelectric module that was not subjected to electroless Ni–P plating, Sn and Te were interdiffused and formed a brittle Sn–Te-based intermetallic compound. The shearing mostly occurred on the bonding interface where such an intermetallic compound was formed. Meanwhile, it was found from the analysis of the bonding interface of thermoelectric module subjected to electroless Ni–P plating that the electroless Ni–P plating acted as an anti-diffusion layer, preventing the interdiffusion of Sn and Te. Therefore, by forming such an anti-diffusion layer on the surface of the thermoelectric element, the bonding strength of the thermoelectric module could be enhanced.

REFERENCES

[1] F.J. Disalro, Science **285**, 703-706 (1999).
[2] D.Y. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannewurf, M. Bastea, C. Uher, M.G. Kanatzidis, Science **287**, 1024-1027 (2000).
[3] K.T. Kim, S.Y. Choi, E.H. Shin, K.S. Moon, H.Y. Koo, G.G. Lee, G.H. Ha, Carbon **52**, 541-549 (2013).
[4] K.T. Kim, I.J. Son, G.H. Ha, J. Kor. Powd. Met. Inst. **20** (5), 345-349 (2013).
[5] M.S. Park, H.Y. Koo, G.H. Ha, Y.H. Park, J. Kor. Powd. Met. Inst. **22** (4), 254-259 (2015).
[6] H. Wada, K. Takahashi, T. Nishizaka, J. Mater. Sci. Lett. **9**, 810-812 (1990).
[7] D. Vasilevskiy, F. Roy, E. Renaud, R.A. Masut, S. Turenne, Proc. 25th Int. Conf. on Thermoelectrics, Vienna, Austria, 666-669 (2006).
[8] T.Y. Lin, C.N. Liao, Albert T. Wu, J. Electron. Mater. **41** (1), 153-158 (2012).
[9] S.W. Chen, C.N. Chiu, Scripta Mater. **56**, 97-99 (2007).