Bondability of Mg$_2$Si element to Ni electrode using Al for thermoelectric modules

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Abstract. The purpose of this study has been to develop a low cost bonding technique for thermoelectric Mg$_2$Si/Si-Ge modules that provides reliable bonding. Aluminum was chosen as an alternative material to conventional silver alloy braze because of its cost advantage and bondability. The shear strength of an aluminum joint between a Mg$_2$Si element and nickel electrode was 19 MPa. The generation capacity of a prototype Mg$_2$Si/Si-Ge twin couple module was about 20% higher than that of a conventional Si-Ge/Si-Ge twin couple module at 923 K ($\Delta T = 620$ K).

1. Introduction

The use of renewable energy resources such as sunlight, water flow and wind is expected to provide an alternative to fossil fuels with the aim of reducing CO$_2$ emissions [1-3]. Power generation from heat recovery, where electricity is generated from the recovery of exhausted heat, has also advanced for the same reason. Thermoelectric generation is one such technology for heat energy recovery. Thermoelectric modules can directly convert heat energy into electrical energy [4]. However, these modules have only been used in special applications, such as satellite power supply [5], because of their high cost and low conversion rate to electricity.

A thermoelectric generation system offers many advantages, including ease of maintenance, because of its simple structure and lack of moving parts. Therefore, many researchers have developed thermoelectric elements with higher conversion efficiencies using super lattice structures, nanocrystals, and new structure modules [6-14].

A thermoelectric module can improve the mileage of a vehicle by utilizing its exhaust heat. However, applying a thermoelectric generator in vehicles presents many challenges, such as the need to reduce heat stress in the bonding region between the thermoelectric element and electrodes, to develop a refractory structure for the thermoelectric module, and to develop a low cost and durable thermoelectric generator that can accommodate a wide range of operating temperatures.

We have previously reported that a Si-Ge thermoelectric element and electrode can be bonded with high reliability using low cost aluminum [15,16]. In this study, we have performed fundamental research focused on an aluminum diffusion bonding technique for mid- to high-temperature (about 573–873 K) thermoelectric modules, specifically the use of aluminum for bonding a Mg$_2$Si
thermoelectric element to a nickel electrode. A prototype Mg$_2$Si/Si-Ge twin couple module was then assembled to evaluate the power generation of this thermoelectric module.

2. Experimental details

2.1. Bonding conditions

Table 1 shows the bonding conditions between the thermoelectric element and electrodes. Aluminum foil of 99% purity was selected as the bonding material. Mg$_2$Si was chosen as the thermoelectric element for this research because it has a better conversion rate than Si-Ge from about 573 K to 873 K. Nickel was selected as the electrode material because its coefficient of thermal expansion (CTE) is 13.4 ppm/K, which is close to that for Mg$_2$Si (15.5 ppm/K). No. 1 and 2 were chosen as low pressure bonding (6.1 × 10$^3$ Pa), and No. 3 was chosen at high pressure bonding (3.0 × 10$^7$ Pa). In addition, with No. 2, the Mg$_2$Si surface was polished before bonding. Further, the Mg$_2$Si element is close to the aluminum foil under high pressure (3.0 × 10$^7$ Pa). The eutectic reaction of aluminum, magnesium and silicon is lower than the melting point of pure aluminum. Consequently, the Mg$_2$Si element and nickel electrode can be joined at temperatures below the melting point of pure aluminum due to interface interdiffusion between Mg$_2$Si and aluminum. In addition, aluminum and nickel produce an Al-Ni intermetallic compound with a high melting point of over 1127 K. These Al-Ni intermetallic compound layers show great promise as a high-melting-point joint between the Mg$_2$Si element and nickel electrode after bonding. Therefore, bonding temperature of test No. 3 was 893 K lower than the melting point of aluminum.

Figure 1 provides a schematic view of the bonding process and also shows the specimen size. The surface of each material was cleaned with acetone. After cleaning, the aluminum foil was then placed between the nickel electrode and Mg$_2$Si element, with the bonding process being performed in the chamber under an atmosphere of pure nitrogen. The bonding pressure was set to either 6.1 × 10$^3$ Pa or 3.0 × 10$^7$ Pa, and the temperature of the hotplate was set to 953 or 893 K for 60 s.

2.2. Shear strength test

Figure 2 presents a schematic view of the shear test for the Mg$_2$Si element/aluminum joint/nickel electrode thermoelectric structure. The nickel electrode was held on a shear tester stage, and the test was executed with a shear speed of 50 μm/s and shear height of 200 μm. The available loading range was under 1000 N. Strength was then calculated by dividing the measured shear strength by 3.7 × 3.7 mm$^2$.

2.3. Metallurgical observation

Characterization of the Mg$_2$Si to nickel joints made with aluminum was conducted by field emission-scanning electron microscopy (FE-SEM). Cross-sections of the bonding interface were prepared after the joint sample was first polished with polishing papers and diamond paste. FE-SEM observations and quantitative analysis by energy-dispersive X-ray spectroscopy (EDX) were then performed.

| No. | Jointing material | Thickness (μm/s) | Device | Elect | Material | Surface condition | Atmosphere | Ramp temp. Rate (K/s) | Max. Temp. (K) | Holding time (s) | Pressure (Pa) |
|-----|------------------|------------------|--------|-------|----------|-------------------|------------|----------------------|--------------|-----------------|--------------|
| 1   | Al-foil          | 25               | Ni     | Mg$_2$Si | Polishing | N$_2$           | As is     | 1                    | 953          | 60              | 6.1 × 10$^3$ |
| 2   | As is            |                  |        |        |          |                  |           |                      |              |                 |              |
| 3   | As is            |                  |        |        |          |                  |           |                      | 893          |                 | 3.0 × 10$^7$ |
3. Results and discussion

3.1. Bondability of the Mg$_2$Si element and nickel electrode with aluminum.

Figure 3 shows the results of the shear tests under each set of bonding conditions. The test number corresponds to bonding conditions 1, 2 or 3 in Table 1. From this, it is evident that No. 1 produced the lowest strength, whereas No. 3 produced the greatest strength. In the case of the latter, the shear strength of the joint between the Mg$_2$Si element and nickel electrode was 19 MPa.

Figure 4 shows cross-sectional views of the bonding interface between the Mg$_2$Si device and nickel electrode before and after the shear tests. The chart numbers correspond to the test numbers in Figure 3. Typically, an oxide film is present on the bonding surface, thus reducing its wettability and bondability [17]. However, a good joint without a discernible gap was confirmed under a bonding pressure of $6.1 \times 10^{-3}$ Pa in the bonding of a Si-Ge element and aluminum foil without flux [15,16]. As shown in Figure 4, a gap exists in No. 1 at the interface between the Mg$_2$Si element and aluminum even before the shear test. In addition, the observation of a flat Mg$_2$Si surface indicates that Mg$_2$Si does seem not to react with molten aluminum. This is probably caused by the reduced wettability resulting from the magnesium oxide layer on top of the Mg$_2$Si element. Also, from the cross-sectional view of Figure 4 No. 2 (Surface treated Mg$_2$Si element), a wavy interface is evident between the Mg$_2$Si element surface and aluminum joint. This can be inferred to mean that the Mg$_2$Si was partially dissolved by molten aluminum. However, a horizontal streaky gap exists in the aluminum joint from the cross sectional view before shear testing. This means that it is the newly formed surface of the Mg$_2$Si that reacts with molten aluminum, as the partial oxide film on the Mg$_2$Si surface is broken by the bonding pressure and the flow of molten aluminum. On the other hand, the oxide film remained as part of the aluminum joint, at a site distant from the Mg$_2$Si surface. Considering these results, the streaky gap in the aluminum joint was most likely formed by this residual oxide film.

Even with a surface-treated Mg$_2$Si element, the Mg$_2$Si surface is re-oxidized well before the bonding process between Mg$_2$Si and aluminum. As shown in Figure 4 No. 2 and Figure 5 (b), the Mg$_2$Si element/aluminum joint/nickel electrode structure is broken at the partially destroyed oxide film. Nevertheless, the joint between the Mg$_2$Si element and nickel electrode separates easily at the streaky gap part of the aluminum joint.

In contrast, in the case of No. 3, a streaky gap was not observed in the cross-sectional view of the joint between the Mg$_2$Si element and nickel electrode. This is probably a result of the oxide film and molten aluminum being discharged at the same time in the direction of the edge by the high bonding pressure ($3.0 \times 10^7$ Pa), thus preventing a streaky gap from being generated. In addition, observation of the cross-sectional view after shear test showed that the Mg$_2$Si element/nickel electrode bonding
structure created using aluminum was broken in the Mg$_2$Si element. Thus, the joint between Mg$_2$Si element and nickel electrode of No. 3 has a high strength without a gap.

Furthermore, the No. 3 joint formed layers on an Al-Ni intermetallic compound (IMC) that included magnesium and silicon. It therefore seems reasonable to assume that the Mg$_2$Si elements were partially dissolved by the molten aluminum.

3.2. Power generation with a prototype Si-Ge/Mg$_2$Si hybrid module
A prototype Si-Ge/Mg$_2$Si twin couple module was bonded based on the results of the shear tests. Specifically, No. 3 of Table 1 was chosen as a reliable bonding condition. A Si-Ge element was used as the P-type semiconductor, and an N-type Mg$_2$Si element was used as the other leg. However, given that the CTE of Si-Ge (3.5 ppm/K) is very different to that of Mg$_2$Si (15.5 ppm/K), we prepared a molybdenum/nickel hybrid electrode to enable CTE matching between the thermoelectric element and electrode. Figure 6 shows an exterior view of the prototype Si-Ge/Mg$_2$Si twin couple module. The bondability of a Si-Ge element and molybdenum electrode using aluminum is discussed elsewhere [15,16].

Figure 7 shows the output power generation of the prototype Si-Ge/Mg$_2$Si twin couple module with the upper electrodes at 923 K and the lower electrodes at 303 K ($\Delta T = 620$ K). A power generation of $1 \text{ W/cm}^2$ was successfully achieved without incurring any damage to the module. This is 20% higher than the power generation of a Si-Ge/Si-Ge twin couple module, and thus a Si-Ge/Mg$_2$Si hybrid module clearly provides a significant improvement at mid- to high-temperature ranges.

![Figure 3](image-url)  
**Figure 3.** Results of shear strength tests between the Mg$_2$Si element and nickel electrode (‘n’ is the number of samples for each test condition).
| No. | Before Shear test | After Shear test |
|-----|-------------------|------------------|
|     |                   | Overall view     | Area 1          |
| 1   | ![Image](image1)  | ![Image](image2) | ![Image](image3) |
| 2   | ![Image](image4)  | ![Image](image5) | ![Image](image6) |
| 3   | ![Image](image7)  | ![Image](image8) | ![Image](image9) |

**Figure 4.** Cross-sectional views of the bonding interface between the Mg$_2$Si device and Ni electrode.

**Figure 5.** Comparison of fracture mode (a) No polishing of the Mg$_2$Si surface and low pressure ($6.1 \times 10^3$Pa) bonding, (b) Polishing of the Mg$_2$Si surface and low pressure ($6.1 \times 10^3$Pa) bonding, (c) No polishing of the Mg$_2$Si surface and high pressure ($3.0 \times 10^7$Pa) bonding.
4. Conclusions

Aluminum foil was used as an alternative bonding material for a Mg$_2$Si element and nickel electrode because of its low cost and high bonding ability. The shear strength of the joint obtained was found to be sufficiently reliable when high pressure bonding was performed. In addition, a highly refractory joint was formed due to the formation of a high-melting-point Al-Ni layer that included magnesium and silicon. A prototype Si-Ge/Mg$_2$Si twin-couple module was subsequently bonded based on the results of the shear tests. Our main findings can be summarized as follows:

- The shear strength of the aluminum joint between the Mg$_2$Si element and Ni electrode under a bonding pressure of $3.0 \times 10^7$ Pa was 19 MPa, which is well above the target value of 10 MPa.
- The generating capacity of the prototype Si-Ge/Mg$_2$Si twin couple module was 1 W/cm$^2$ at $\Delta T = 620$ K (high temperature side: 923 K), or 20% higher than that of a Si-Ge/Si-Ge twin couple module.

References

[1] Arvizu D and Balaya P 2011 *IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation* 33
[2] Hayami H, Nakamura M and Yoshioka K 2005 *IEEE Trans. on Systems Man and Cybernetics Part C Applications and Reviews.* 35 391
[3] Tagare D 2011 *Electricity Power Generation: The Changing Dimensions:* 173
[4] Rowe D 2012 *Thermoelectrics and its energy harvesting* 1st edition, (CRC press) 1-2
[5] Anderson D J, Sankovic J, Witt D and Abelson R D 2007 *Proc. of aerospace conference (montana, USA, 3-10 March 2007)* 1
[6] Venkatasubramanian R, Siivola E, Colpitts T and Oquinn B 2001 *Nature* 413 597
[7] Poudel B, Hao Q, Ma Y, Lan Y C, Minnich A, Yu B and Yan X 2008 *Science* 320 634
[8] Miyazaki K 2008 *OYO BUTURI* 78 527
[9] Tanaka S, Takashiri M and Miyazaki K 2010 *Jpn. Journal of Thermophysical Properties* 24 94
[10] Kaibe H, Aoyama I, Mukoujima M, Kanda T, Fujimoto S, Kurosawa T, Ishimabushi H, Ishida K, Rauscher L, Hata Y and Sano S 2005 *Proc. of 24th International Conference on Thermoelectrics (South Carolina, USA 19-23 June 2005)* 242

**Figure 6.** Exterior view of a prototype Si-Ge/Mg$_2$Si twin-couple module.

**Figure 7.** Power generation of the prototype module (upper and lower electrode $\Delta T = 620$ K).
[11] Crane D T, Lagradeur J W, Harris F and Bell L E 2009 Journal of Electronic Materials 38: 1375
[12] Kambe M, Jinushi T and Ishijima Z 2011 Journal of Electronic Materials 39 1418
[13] Lin W P and Lee C C 2011 Proc. of IEEE 61th ECTC (Florida, USA, 31 May-3 June 2011) 118
[14] Ishii K 2013 Hitachi Chemicals Technical Report 55 50
[15] Fujiwara S, Tohei T, Jinushi T and Ishijima Z 2012 Proc. of 4th ESTC(Amsterdam, Netherlands, 17-20 September 1993 ) 1
[16] Tohei T, Fujiwara S, Jinushi T and Ishijima Z 2013 J. Jpn. Soc. Powder Powder Metallurgy 60 360
[17] Jpn.Weld. Soc. 2003 YOSETSU SETSUGO handbook 2nd edition (Maruzen) 434