Journal of ELECTRONIC MATERIALS, Vol. 43, No. 6, 2014
DOI: 10.1007/s11664-013-2910-7

Evaluation of the Thermoelectric Module Consisting of W-Doped Heusler Fe_2VAl Alloy

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Power generation performance of a thermoelectric module consisting of the Heusler Fe_2VAl alloy was evaluated. For construction of the module, W-doped Fe_2VAl alloys were prepared using powder metallurgy process. Power generation tests of the module consisting of 18 pairs of *p*–*n* junctions were conducted on a heat source of 373–673 K in vacuum. The reduction of thermal conductivity and improvement of thermoelectric figure of merit by W-doping enhanced the conversion efficiency and the output power. High output power density of 0.7 W/cm^2 was obtained by virtue of the high thermoelectric power factor of the Heusler alloy. The module exhibited good durability, and the relatively high output power was maintained after temperature cycling test in air.

Key words: Thermoelectric module, Heusler alloy, powder metallurgy, power generation

INTRODUCTION

Thermoelectric devices have recently attracted renewed interest for their potential application in clean energy-conversion systems. Especially, vast amounts of low-temperature waste heat, such as that less than 600 K, are targeted for thermoelectric power generation because such low-temperature heat energy is difficult to reuse with other energy conversion systems. The conversion efficiency of a thermoelectric device depends mainly on the material's thermoelectric properties, which are evaluated using the thermoelectric figure of merit Z ($=S^2/\rho\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity). A Bi-Te system is one of the major materials for use in low-temperature thermoelectric devices.[1] Although the Bi-Te thermoelectric device has good energy conversion efficiency, it seems to have run into difficulty for widespread use because of the higher cost and the limited supply of raw materials. In addition, the low resistance to oxidation and the poor mechanical strength of Bi-Te alloy make the construction of a durable thermoelectric device difficult.

A Heusler alloy, Fe_2VAl, is a promising candidate for thermoelectric power generation near room temperature because of its high power factor PF ($=S^2/\rho$), such as 5.4 mW/mK^2 at 300 K.[2] In a Fe_2VAl system, the enhancement of PF and the control of conduction type can be realized simultaneously by partial element substitution, such as Si for the Al site for *n*-type and Ti for the V site for *p*-type.[2,3] Therefore, a thermoelectric module consisting only of the Fe_2VAl system can be fabricated.[4] Furthermore, because of its high mechanical strength and excellent resistance to oxidation and corrosion, a durable thermoelectric module can be fabricated using this alloy. Moreover, the Heusler alloy comprises predominantly abundant chemical elements such as Fe and Al and contains no toxic elements. The high durability and abundance of the material can be advantageous for the construction of reliable thermoelectric devices. The widespread use of this material for thermoelectric generation systems is anticipated.

(Received June 27, 2013; accepted November 6, 2013; published online November 26, 2013)

An important shortcoming of the Fe_2VAl alloy is its high κ of approximately 28 W/mK,[5] resulting in a low Z value. Consequently, its thermoelectric energy conversion efficiency is much lower than that of state-of-the-art thermoelectric materials. Reduction of κ is therefore necessary for practical applications. In an earlier study, we fabricated Fe_2VAl material with reduced grain size, and demonstrated that boundary scattering effectively reduced κ.[6] In addition, for further reduction of κ, we doped a heavy element of W into the Heusler Fe_2VAl structure to achieve a κ reduction effect within grains by the mass-difference scattering in the crystal lattice.[7,8] In this study, to verify the κ reduction effect on power generation performance, a thermoelectric module consisting of W-doped Fe_2VAl sintered alloy was constructed, and its power generation capacity was investigated.

EXPERIMENTAL

Sintered bulk materials of the W-doped Heusler Fe_2VAl alloy (W-FVA) were fabricated using a powder metallurgical process. Alloy powders prepared by mechanical alloying were sintered using pulse-current sintering technique. Details of preparation procedures were described in previous papers.[6–8] As reported in the previous paper, the n-type Fe_2VAl alloy is obtainable by the electron-doping effect resulting from W substitution for the V site.[7] To obtain a p-type alloy for the construction of thermoelectric module, holes were doped into the W-substituted Fe_2VAl alloy by the additional Ti substitution for the V site.[8] For the construction of thermoelectric modules, bulk material having a cubic-like shape with a typical size of 2 × 2 × 3 mm was used. The cubic-like shaped sintered materials were connected with a copper electrode. Details of the process for producing a Fe_2VAl thermoelectric module were described in a previous paper.[4]

The ρ of the sintered alloys was measured in a He atmosphere between 350–750 K using a conventional four-probe DC technique. S was calculated from a plot of thermoelectric voltage against the temperature difference. κ was evaluated using the laser flash method. The electricity-generating capacity of the thermoelectric module consisting of 18 pairs of p–n junctions was measured by changing the load resistance using an electronic load system in vacuum. One side of the thermoelectric module was heated using a heat source of 373–673 K and the other side was cooled using a heat sink of 293 K. Output power (P) was calculated from measured output voltage (E) and current (I). Efficiency (η) is defined from P and the heat flow from the cold side of the module. Details of measurement system were described in a previous paper.[9] The durability of the thermoelectric module against temperature cycling in the range of 330–573 K was evaluated in air. The heating and cooling rate was 60 and 15 K/min, respectively. The power generation capacity was measured during 10 min holding at 573 K in each temperature cycle.

RESULTS AND DISCUSSION

Figure 1 presents the temperature dependence of S and ρ in the sintered alloys. The reported band-structure calculations suggest that the Fe_2VAl is a semimetal with a steep pseudogap at the Fermi level.[10,11] Since the Fermi level lies around the bottom of pseudogap, S produced by electrons and holes are expected to nearly neutralize each other, resulting in a small value of S of less than 30 μV/K in the non-substituted Fe_2VAl alloy.[2,3] A large negative S value was obtained by the W substitution resulting from the electron doping because the number of valence electrons of W is greater than that of V. The obtained S value in the W-substituted sample is as high as that in the $Fe_2VAl_{0.9}Si_{0.1}$, which has been reported as a conventional n-type Heusler alloy.[2] For the additionally Ti-substituted sample, the valence electron density is reduced and the Fermi level can be shifted from a conduction-band to a valence-band because the number of valence electrons of Ti is lower than that of V. As a result, S was changed to a positive value. The S value in the sample with the double substitution of W and Ti is as high as that in the $Fe_2V_{0.9}Ti_{0.1}Al$, which has been reported as a conventional p-type Heusler alloy.[3]

The non-substituted Fe_2VAl exhibits a semiconductor-like T dependence of ρ over a wide temperature range up to 1,200 K and its value reaches 3 mΩcm at 2 K.[12] Although ρ decreases with the increase in T, its value is still as high as 1 mΩcm at 300 K. Compared to the non-substituted Fe_2VAl alloy, the ρ value was reduced by the element substitution and its T dependence was changed to metallic-like behavior as presented in Fig. 1. This reduction of ρ can be explained simply by the carrier-doping effect achieved via the element substitutions, as expected from the difference in the nominal valence of V and substitution elements of W and Ti. The reduced ρ values in the n-type and p-type W-FVA are as low as that in the reported

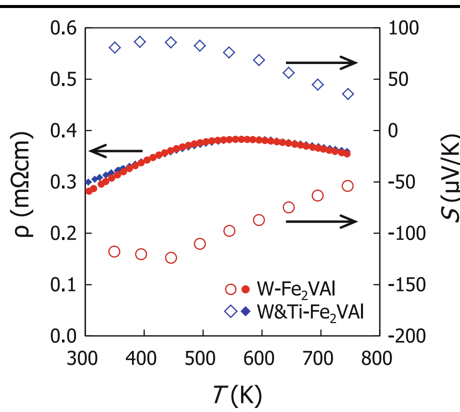

Fig. 1. T dependence of S and ρ in the n-type solo W-substituted and in the p-type W and Ti-substituted Fe_2VAl sintered alloy.

carrier-doped Heusler Fe_2VAl alloys, such as the n-type $Fe_2VAl_{0.9}Si_{0.1}$ and p-type $Fe_2V_{0.9}Ti_{0.1}Al$.[2,3] On the other hand, compared to the κ value in the conventional n-type Si-substituted and p-type Ti-substituted Fe_2VAl sintered alloy of 12 and 14 W/mK, respectively, the W-FVAs exhibit a much lower κ value of 7 W/mK at room temperature. This great reduction of κ without severe deterioration in electrical properties contributed to the enhancement of Z. Details of the W-substitution effects on the thermoelectric properties of Fe_2VAl alloy were described in previous papers.[7,8]

The power generation capacity of the thermoelectric module consisting of the W-FVA was evaluated. The power generation test was performed using the thermoelectric module consisting of 18 pairs of p–n junction (Fig. 2). As depicted in Fig. 3, E and P values increase with the increasing the heat source temperature (T_H). The maximum output power (P_{max}) at $T_H = 673$ K reaches 2.1 W. Because the heat-receiving area of this module is about 1.7 × 1.7 cm, the output power density is estimated to be 0.7 W/cm^2, which is comparable to that of the Bi-Te thermoelectric module. In addition, η also increases with the increase of T_H and its value reaches 1.4%. The results of the power generation test are summarized in Table I.

Figure 4 shows comparisons of measurement results and calculated η and P_{max} from the thermoelectric properties of W-FVA. Measured values are much lower than expected. Usually, one reason accounting for the degradation in η and P_{max} is interfacial electrical resistance between the thermoelectric element and electrode material, which increases the internal resistance (R_i) of the thermoelectric module and causes power loss. However, the actual R_i of 101.9 mΩ calculated from the measured I dependence of E is almost identical to the estimated R_i of 100.4 mΩ calculated from the ρ of W-FVA. Therefore, the power loss by the interfacial electrical resistance can be negligible in our module. The other cause of the degradation of the results of the power generation test is the thermal resistance between the thermoelectric module and heat sources. For the power generation test, an insulating 1-mm-thick AlN plate was inserted between the bare electrode thermoelectric module and the metallic heat source or heat sink to prevent electrical leakage. Although the thermal conductivity of the AlN plate is relatively high, such as 195 W/mK, and although thermal conductive paste was applied between each solid part, the thermal resistance is unavoidable even though 5 MPa pressure was applied to enhance the thermal contacts, resulting in a severe temperature drop between the heat source (sink) and the thermoelectric element. Actually, the estimated temperature difference at the thermoelectric element (dT_{est}), which is calculated from the open circuit voltage (E_{OC}) and S of the sintered alloys, is much lower than the temperature difference (dT) between the heat source and heat sink as listed in Table I. Then, the generation power, which increases with the square of dT, is considerably reduced. The thermal conductivity of the AlN plate and the constituent materials of the heat source and heat sink is high compared to the thermoelectric element. Therefore, the main cause of the temperature drop is poor thermal contact among the solid parts. Simple heat conduction analysis shows that about 90% of the temperature drop is attributable to the interfacial thermal resistance. In addition, direct thermal radiation from heat source to heat sink also caused the reduction of power generation performance because the distance between the hot side and cold side is as small as 4 mm.

Measured η and P_{max} of a thermoelectric module consisting of the conventional Fe_2VAl alloys of n-type $Fe_2VAl_{0.9}Si_{0.1}$ and p-type $Fe_2V_{0.9}Ti_{0.1}Al$ sintered alloy with the same configuration are portrayed in Fig. 4. It is readily apparent that improvement of the Z value by W-doping enhances η. In addition, the κ reduction effect by the W-doping enhanced dT, thereby improving E and P. The dT_{est} in the W-FVA module is about 10 % larger than that in the module consisting of the conventional Fe_2VAl sintered alloys without W-doping. This effect contributes indirectly to η enhancement.

To evaluate the geometric effect on the power generation performance, the element height (H)

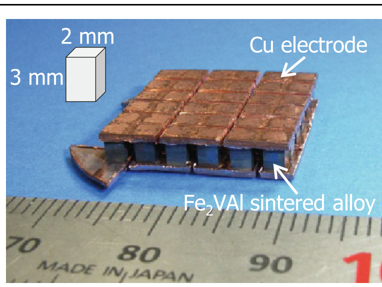

Fig. 2. Thermoelectric module consisting of 18 pairs of p–n junctions.

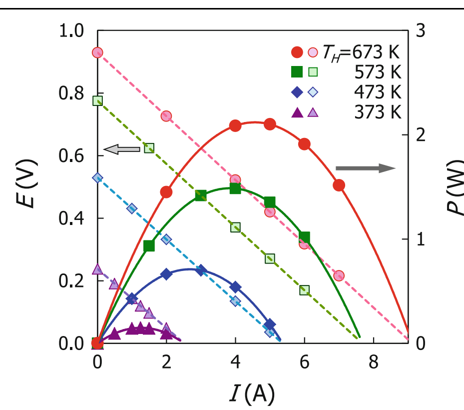

Fig. 3. E and P of the W-FVA thermoelectric module.

Table I. The power generation capacity of the W-FVA thermoelectric module

T_H (K)	dT_{est} (K)	E_{OC} (V)	P_{max} (W)	PMD (W/cm^2)	n (%)
373	70	0.24	0.15	0.05	0.5
473	145	0.53	0.71	0.25	1.0
573	215	0.78	1.49	0.51	1.3
673	275	0.93	2.12	0.73	1.4

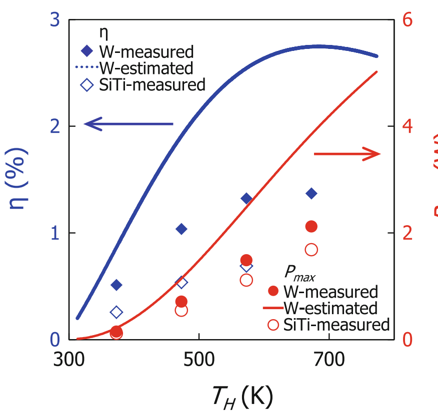

Fig. 4. η and P_{max} of the thermoelectric module consisting of the W-FVA and the conventional n-type Si-substituted and p-type Ti-substituted Fe_2VAl alloy. The estimated P_{max} and η of the W-FVA thermoelectric module are also indicated.

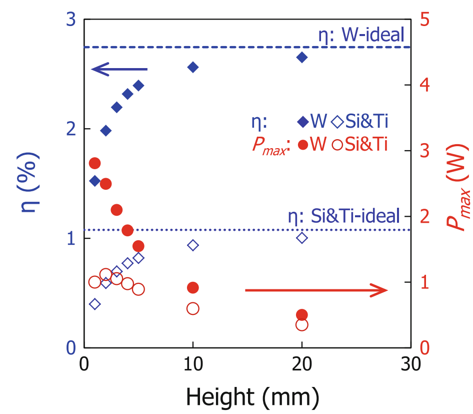

Fig. 5. Element height dependence of η and P_{max} of the thermoelectric module consisting of W-FVA and the conventional n-type Si-substituted and p-type Ti-substituted Fe_2VAl alloy.

dependence of η and P_{max} at T_H = 673 K is estimated as presented in Fig. 5. For estimation, the module configuration, except for the element height, was fixed, and the interfacial thermal resistance estimated from the above power generation test was taken into account. η is enhanced by the increase of H. This enhancement of η results from the increase of dT at the thermoelectric element, resulting from the increase of thermal resistance at the thermoelectric element and the relative decrease in the interfacial thermal resistance. At H = 20 mm, η of the W-FVA thermoelectric module reaches 97 % of ideal η, which is calculated without the interfacial thermal resistance effect. On the other hand, P_{max} increases with the decrease of H because of the reduction of electrical resistance at the thermoelectric element. At H = 1 mm, P_{max} of the W-FVA thermoelectric module reaches 2.8 W, which corresponds to the power density of 1.0 W/cm^2. It is particularly interesting that the rate of increase in P_{max} in the conventional Fe_2VAl thermoelectric module by the decrease of H is lower than that of the W-FVA thermoelectric module. Moreover, P_{max} in the conventional Fe_2VAl thermoelectric module decreases with the decrease of H below 2 mm. This degradation of P_{max} results from the higher κ of the conventional Fe_2VAl alloy, resulting in the lower dT at the thermoelectric element. These results indicate that the reduction of κ by the W-doping improves both η and P_{max} in practical thermoelectric power generation.

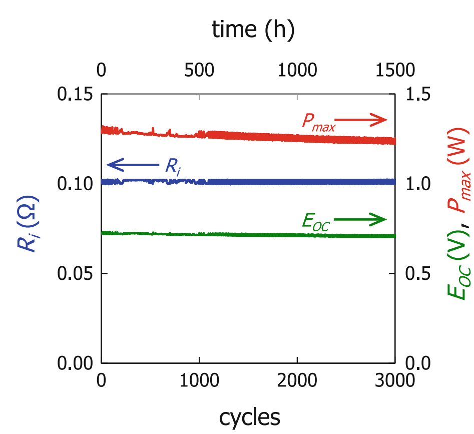

Fig. 6. R_i, E_{OC} and P_{max} of the W-FVA thermoelectric module under temperature cycle test.

The power generation performance of the thermoelectric module against temperature cycling in the range of 330–573 K was evaluated as presented in Fig. 6. Through the 3,000 times (1,500 h) temperature cycling, the R_i value is almost constant. This result suggests that the electrode joint and the Fe_2VAl alloy are highly resistant to rapid temperature change and oxidation in air at 573 K. On the other hand, the P_{max} value decreased gradually because of the reduction of E. We suppose that the decrease in E was mainly caused by the reduction of dT at the thermoelectric element resulting from the increase of thermal resistance between the module and heat source because the thermal conductive paste is the most deteriorative material among the power generation components. This temperature cycling test is still ongoing and will continue until 10,000 cycles (5,000 h). The detailed investigation of the cause of the reduction of E will be conducted after the test.

CONCLUSIONS

A thermoelectric module consisting of W-doped Heusler Fe_2VAl sintered alloy was fabricated. The reduction of κ by the heavy element W-doping improves both η and P when taking account of practical interfacial thermal resistance. The power density of 0.7 W/cm^2 on the heat source of 673 K is comparable to that of a state-of-the-art thermoelectric module: 1 W/cm^2 for a Bi-Te module.[13] We expect that the low-cost constituent element and the high durability of the Heusler alloy will provide many benefits in practical applications.

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