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DEVELOPMENT OF HEUSLER-TYPE Fe_2VAl ALLOYS FOR THERMOELECTRIC POWER GENERATION

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Abstract

A Heusler alloy, Fe_2VAl, is a promising candidate for thermoelectric power generation because of its high thermoelectric power factor, such as 5.5 mW/mK^2 at 300 K. This high power factor is produced by a steep pseudogap around the Fermi level. The simultaneous enhancement of Seebeck coefficient and electrical conductivity can be achieved by the control of valence electron concentration within a rigid band model. Moreover, recent studies in the off-stoichiometric composition control, such as $Fe_{2-x}V_{1+x}Al$, suggest that the modification of the electronic band structure can further enhance the Seebeck coefficient, resulting in the higher power factor. The power generation ability was evaluated by the construction of a thermoelectric module consisting of only the Fe_2VAl alloy. A high output power density of 0.7 W/cm^2 was then obtained. The durability of the Fe_2VAl module derived from high mechanical strength and excellent resistance to oxidation enhances utility for practical thermoelectric power generation.

Introduction

Thermoelectric materials have recently attracted renewed interest for their potential application in clean energy-conversion systems. For instance, vast amounts of waste heat are targeted for thermoelectric power generation. The efficiency of thermoelectric materials is 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 Heusler-type intermetallic compound Fe_2VAl is a promising candidate for thermoelectric power generation near room temperature because of its high thermoelectric power factor PF (= S^2/ρ, which is used to estimate the power generation ability of thermoelectric material) [1]. In the Fe_2VAl system, it is suggested that the high PF value, the coexistence of large S and low ρ, is produced by a steep pseudogap at the Fermi level [2, 3].

Reported electronic-structure calculations consistently agree with the formation of pseudogap at Fermi level of Fe_2VAl system [4-8]. A nuclear magnetic resonance study and optical conductivity measurements has experimentally confirmed the existence of steep pseudogap of 0.1~0.27 eV around Fermi level [9, 10]. In the metallic system, S at temperature T is often discussed using the well-known formula [11],

$$S(T) = \frac{\pi^2}{3}\frac{k_B{}^2}{(-e)}T\left(\frac{\partial \ln\sigma(E)}{\partial E}\right)_{E=E_\mathrm{F}}, \tag{1}$$

where σ(E) is the electrical conductivity and E_F represents the Fermi energy. Provided σ(E) is proportional to the density of states (DOS) $N(E)$, it is argued that a large S is brought about by a low $N(E)$ coupled with its steep slope, $\partial N(E)/\partial E$, near E_F. Thus we expect the S of Fe_2VAl system to be well enhanced by shifting of E_F to a sharply rising portion of DOS, where the both sides of the pseudogap, resulting from doping or off-stoichiometry. In addition, the narrow pseudogap and residual density of state support the high σ required to achieve a large *PF*. Indeed, a variety of Fe_2VAl-based thermoelectric materials both p-type and n-type with the relatively high *PF* value have been developed [1-3, 12].

For the practical application, low κ value is indispensable for achieving high thermoelectric performance. However, intrinsic κ value in Fe_2VAl of 28 W/mK is one order higher than the state-of-the-art thermoelectric materials, resulting in the low Z value. In the Fe_2VAl system, κ is mainly governed by the lattice part of κ. Then, the enhancement of phonon scattering by the introduction of crystal lattice defects or grain boundaries is effective to reduce the total κ. Indeed, the appreciable reduction of κ by the heavy-element doping [3, 13-15] or the microstructure refinement [16], without a serious deterioration of electronic properties, improved the Z value of the Fe_2VAl material.

From the practical view point, because of its high mechanical strength and excellent resistance to oxidation and corrosion of Fe_2VAl alloy, a durable thermoelectric module can be fabricated using this alloy [17, 18]. Moreover, the Fe_2VAl alloy is predominantly comprised of abundant chemical elements such as Fe and Al and contains no toxic elements. The high durability and abundance of the material could be advantageous for the widespread use of this material as a thermoelectric power generation system. In this paper, we survey our recent studies concerning the thermoelectric properties of the pseudogap Fe_2VAl system, focusing on the doping and off-stoichiometric effect, and the development of a thermoelectric module for power generation from low temperature waste heat.

Thermoelectric Properties of the Heusler Fe_2VAl alloy

Seebeck Coefficient

In Fig. 1, S for $Fe_2VAl_{1-x}Si_x$ with $0 \leq x \leq 0.10$ and $Fe_2V_{1-y}Ti_yAl$ with $0 \leq y \leq 0.10$ are shown as a function of temperature [1, 12]. While the value of S for Fe_2VAl (x, $y = 0$) is less than 30 μV/K over the whole temperature range examined, the $|S|$ value increases remarkably with increasing the substitution amount x or y, reaching S of −130 μV/K at 300 K for $x = 0.05$ and S of 70 μV/K at 400 K for $y = 0.05$. On the basis of the rigid band model, the Si substitution leads to the electron doping effect and corresponding upward shift of the Fermi level because the DOS within the pseudogap is very small. This Fermi level shift from the bottom of pseudogap to a conduction-band having a sharply rising DOS can contribute to the development of the large S value according to equation (1), which suggests that the value of S is proportional to the slope of the DOS at Fermi level. For the Ti substitution leading to the hole doping, the same scenario can be applied because the valence-band also has the large slope of the DOS in the Fe_2VAl system.

For the $Fe_2VAl_{1-x}Si_x$, the $|S|$ value increases gradually as the temperature increases, forming a broad maximum, and then turns to decrease. The decrease in $|S|$ at high temperatures could be ascribed to the contribution of thermally excited antitype carriers across the pseudogap, as in the case for semiconductors, and the temperature at which $|S|$ reaches a maximum increases with increasing x. This tendency can also be found in $Fe_2V_{1-y}Ti_yAl$ by the measurement of S at higher temperatures [15].

On the basis of the site selectivity of doping elements, various Fe_2VAl-based thermoelectric materials have been developed [19-25]. We believe that the variation of valence electron concentration (VEC) due to doping is the most important factor for a large enhancement in S. Fe_2VAl has in total 24 valence electrons per formula unit, so that VEC = 6. The sign of S is always positive for the alloys with VEC ≤ 6 but becomes negative for VEC > 6. Consequently, the VEC dependence of S value falls on a universal curve, irrespective of the doping elements [26]. Therefore, a small deviation of VEC from the stoichiometric value of 6 always leads to a large enhancement in S. It is considered that, since the DOS within the pseudogap is very small, even a small compositional change due to doping would result in an appreciable shift of the Fermi level from the central region in the pseudogap without modifying the band structure in any essential manner.

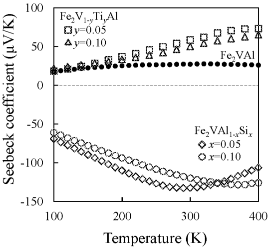

Figure 1. Temperature dependence of Seebeck coefficient in $Fe_2VAl_{1-x}Si_x$ and $Fe_2V_{1-y}Ti_yAl$ with $0 \leq x, y \leq 0.10$

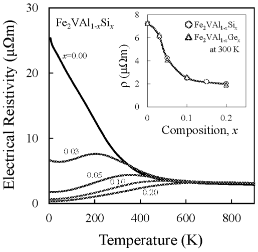

Figure 2. Temperature dependence of electrical resistivity in $Fe_2VAl_{1-x}Si_x$ with $0 \leq x \leq 0.20$. The inset shows the electrical resistivity at 300 K as a function of composition x in $Fe_2VAl_{1-x}Si_x$ and $Fe_2VAl_{1-x}Ge_x$.

Electrical Resistivity

Figure 2 shows the temperature dependence of ρ in $Fe_2VAl_{1-x}Si_x$ with $0 \leq x \leq 0.20$ [1]. The ρ value decreases concomitantly with increased Si content, especially at temperatures less than 600 K. ρ for $x = 0.20$ is reduced to only 0.35 μΩm at 4.2 K, which is almost two orders of magnitude lower than that for non-substituted Fe_2VAl. In addition, the temperature dependence of ρ changes from the semiconductor-like $\partial\rho/\partial T < 0$ dependence to metallic $\partial\rho/\partial T > 0$ behavior. This variation of ρ at low temperatures can be explained by the electron doping effect: the Fermi level shifts from the bottom of pseudogap to conduction band by the Si substitution, as expected from the small DOS around the pseudogap and the difference in the nominal valence of Al and Si. In spite of a significant decrease in the low-temperature ρ, all the ρ curves almost coincide with each other at high temperatures above 600 K.

In order to compare the doping effect, the ρ measured typically at 300 K for $Fe_2VAl_{1-x}Si_x$ and $Fe_2VAl_{1-x}Ge_x$ is plotted in the inset of figure 2 as a function of the composition x [3]. It can be seen that the compositional variation coincides with each other regardless of the doping elements, which is also a positive evidence for a rigid-band-like shift of the Fermi level due to doping of isoelectronic elements. We conclude therefore that both the S and ρ in the pseudogap systems can be controlled by tuning the Fermi level to an energy position at which *PF* value can be maximized without a substantial modification of the electronic structure. It should be remarked that $Fe_2VAl_{1-x}Si_x$ with $x = 0.10$ shows a large *PF* of 5.5 mW/mK^2 at around 300 K [1], which is substantially higher than that of a conventional thermoelectric material Bi_2Te_3.

Off-stoichiometric Effects on Thermoelectric Properties

The effect of off-stoichiometric compositional control on the thermoelectric properties of Fe_2VAl alloy has also been investigated, i.e., $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ [2], $Fe_{2-x}V_{1+x}Al$ [27-29]. For the $Fe_{2-x}V_{1+x}Al$ system, the sign of S becomes negative at a slightly V-rich composition ($x > 0$), and a large enhancement in S is observed in parallel with a drastic increase in the ρ value at low temperatures [27]. The occurrence of a more pronounced semiconducting behavior for the V-rich alloys with $x > 0$ is, however, very different from the $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ system [2] where a small deviation of the Al content always causes a substantial reduction in ρ. Although the off-stoichiometric $Fe_{2-x}V_{1+x}Al$ alloys do exhibit a large S, their large values of ρ make them rather poor thermoelectric materials [27]. We have recently found that not only a large S but also a low ρ can be expected for the off-stoichiometric alloys only by tuning the Fermi level very precisely due to doping [14, 30].

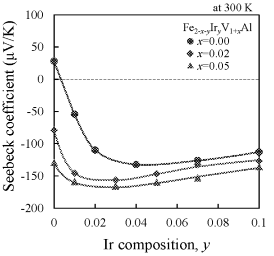

Figure 3. Seebeck coefficient at 300 K in $Fe_{2-x-y}Ir_yV_{1+x}Al$ with $x = 0$, 0.02 and 0.05.

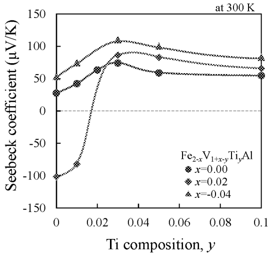

Figure 4. Seebeck coefficient at 300 K in $Fe_{2-x}V_{1+x-y}Ti_yAl$ with $x = -0.04$, 0 and 0.02 as a function of Ti composition y.

Figure 3 shows the S at 300 K in $Fe_{2-x-y}Ir_yV_{1+x}Al$ with $x = 0$, 0.02 and 0.05 as a function of composition y [14]. While a small deviation from the stoichiometric Fe_2VAl composition causes an enhancement in the S value, a slight substitution of Ir for Fe leads to a further increase in the S value, reaching −170 μV/K at 300 K for $x = 0.05$ and $y = 0.03$, which is larger than that of the stoichiometric Fe_2VAl-based alloys so far reported. It is noted here that the doping effect of Ir is almost the same even for the off-stoichiometric alloys. A large enhancement in S of the off-stoichiometric alloys could be due to a modification in the band structure around the Fermi level. Further, the doping of heavier atoms such as Ir reduces more effectively the thermal conductivity, reaching 7 W/mK for $y = 0.10$, while retaining the low ρ as well as the large S, thus resulting in an increased figure of merit of $Z = 8.6\times10^{-4}$ K^{-1} at 300 K.

In order to demonstrate the off-stoichiometric effect for p-type material, figure 4 shows the S value at 300 K in $Fe_{2-x}V_{1+x-y}Ti_yAl$ with $x = -0.04$ and 0.02 as a function of Ti composition y [30]. For the V-rich alloy with $x = 0.02$, the sign of S changes from negative to positive by the Ti substitution, and the S value is substantially larger than the stoichiometric alloy with $x = 0$. This change in the sign of S for the Ti substitution could be caused by a shift of the Fermi level across the bottom of the pseudogap. It can be seen that the S value for the Fe-rich alloy with $x = -0.04$ is always larger than the V-rich alloy, reaching 110 μV/K at 300 K for $y = 0.03$. According to soft X-ray photoelectron spectroscopy, the valence-band spectra near the Fermi level of the Fe-rich alloy with $x = -0.04$ is drastically changed from that of stoichiometric Fe_2VAl, so that substantial enhancements in S could be due to a modification in the band structure on the valence band side around Fermi level [29]. We conclude that a larger S value with a positive sign can be obtained for the Fe-rich alloys rather than the V-rich alloys, while a larger S value with a negative sign is available for the V-rich alloys.

Thermal Conductivity

Thermal conductivity is generally determined by contributions both from conduction electrons and phonons. One of the current challenges is therefore to reduce the lattice part of κ while retaining the low ρ as well as the large S. We fabricated Fe_2VAl material with reduced grain size using mechanical alloying and pulse-current sintering [16]. As shown in Fig. 5, the sintered alloy consisting of submicrometer-sized grains can be obtained. Compared to the intrinsic κ value in Fe_2VAl of 28 W/mK [3], the Fe_2VAl sintered alloy exhibits a much lower κ value of 16 W/mK at room temperature, as shown in Fig. 6. This large reduction of κ is caused by phonon scattering at grain boundaries in the microstructured sintered alloy.

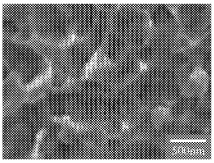

Figure 5. SEM image of the cross-sections of Fe_2VAl sintered alloy.

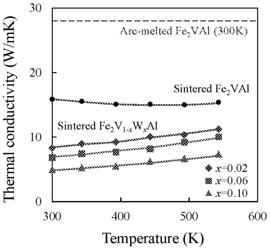

Figure 6. Temperature dependence of thermal conductivity in the $Fe_2V_{1-x}W_xAl$ sintered alloy with $0 \leq x \leq 0.10$. The dashed line is the thermal conductivity of arc-melted Fe_2VAl alloy at 300 K.

In addition, for the further reduction of κ, we doped a heavy element of W into the Heusler Fe_2VAl structure to achieve κ reduction effect within grains by the mass-difference scattering in the crystal lattice [15]. Figure 6 shows that the value of κ decreases concomitantly with the increased W content. The further reduction of κ in the W-substituted samples is then attributed to phonon scattering by point defects resulting from the introduction of W atoms, which have the heavier atomic weight and the larger atomic radius than substituted V atom. When replacing V by W, the electron doping effect can also be expected from the larger number of valence electrons of W than that of V. Therefore, the enhancement of S in parallel with the decrease in the ρ can be achieved by the electron doping as mentioned above. Consequently, ZT value of 0.2 in $Fe_2V_{1-x}W_xAl$ with $x = 0.10$ was obtained.

Fe_2VAl Thermoelectric Module for Power Generation

A thermoelectric module consisting of 18 pairs of p-n junction was constructed using W-doped Fe_2VAl sintered alloy, as shown in Fig. 7. For the construction of thermoelectric modules, bulk material having a cubic-like shape with a typical size of 2 × 2 × 3 mm^3 was used. The cubic-like shaped sintered materials were connected in series with a copper electrode. The most important subject in the fabrication of thermoelectric devices is minimizing the electrical resistance at the electrode joint, which leads to a loss of electrical output. For the Fe_2VAl thermoelectric module, an electrode joint with a negligibly small electrical resistance can be formed by using direct bonding between Fe_2VAl alloy and Cu electrode induced by Joule heating at a high pressure [17]. Indeed, the internal resistance (R_i) of Fe_2VAl module shown in Fig. 7 is 101.9 mΩ. This R_i value is almost identical to the estimated R_i of 100.4 mΩ calculated from ρ of Fe_2VAl sintered alloy. Therefore, the power loss by the electrical resistance at electrode joint was sufficiently suppressed in our module. In addition, the shear strength of the direct bonding was estimated to be 100 MPa. This bonding strength is much higher than that of the solder joint and the enhancement of durability can be expected [18].

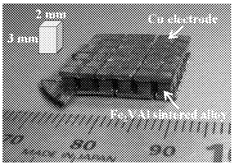

Figure 7. Thermoelectric module consisting of 18 pairs of p-n junctions.

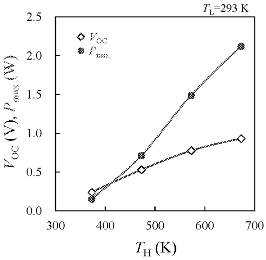

Figure 8. Open circuit voltage (V_{OC}) and maximum output power (P_{max}) of the Fe_2VAl thermoelectric module as a function of the heat source temperature (T_H).

The electricity-generating capacity of the thermoelectric module 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. As depicted in Fig. 8, Open circuit voltage (V_{OC}) 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^2, 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 power generation performance of the thermoelectric module against temperature cycling in the range of 330–573 K was evaluated. Through the 6000 times (3000 hours) 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 thermoelectric element resulting from the increase of thermal resistance between the module and heat source because thermal conductive paste, which is used for the reduction of thermal resistance between thermoelectric module and heat sources, is the most deteriorative material among the power generation components. This temperature cycling test is still ongoing and will continue until 10000 cycles (5000 hours). The detailed investigation of the cause of the reduction of E will be conducted after the test.

Conclusions

The Heusler compound Fe_2VAl having a steep pseudogap around Fermi level possesses a favorable electronic property as a thermoelectric material. The rigid-band-like shift of the Fermi level from the bottom of pseudogap to a sharply rising portion of DOS simultaneously enhances S and σ, resulting in a high PF value. Moreover, the off-stoichiometric $Fe_{2-x}V_{1+x}Al$ alloys with appropriate tuning of Fermi level leads to a further enhancement in the S value, reaching −170 μV/K for the n-type V-rich alloy and 110 μV/K for the p-type Fe-rich alloy. The appreciable reduction of lattice part of κ by the heavy-element doping or the microstructure refinement, without a serious deterioration of electronic properties, improved the Z value of the Fe_2VAl alloy.

A thermoelectric module consisting of Heusler Fe_2VAl sintered alloy exhibits a relatively high power density value of 0.7 W/cm^2, which comparable to that of a state-of-the-art thermoelectric module: 1 W/cm^2 for a Bi-Te module [31]. 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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