Thermal Conductivity in $X_2YZ$ Heusler Type Intermetallic Compounds

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Results are given of comprehensive measurements on thermal conductivity of Heusler type intermetallic compounds Fe$_2$AlTi, Co$_2$AlTi, Ni$_2$AlTi, Ni$_2$GaTi, Ni$_2$AlZr and Ni$_2$AlHi. The compounds have fully ordered L2$_1$ structure. There exists a wide single phase region of L2$_1$ in Ni-Al-Ti ternary alloy system. The contour map showing the magnitude of thermal conductivity is constructed in Ni$_2$Ti single phase region. The thermal conductivity in Ni$_2$AlTi takes a maximum of 21.4 Wm$^{-1}$K$^{-1}$ at stoichiometry which is much lower than that of NiAl having a B2 structure. By the deviation from stoichiometry, the thermal conductivity decreases in Heusler compounds. The magnitude of thermal conductivity in Fe$_2$AlTi, Co$_2$AlTi and Ni$_2$AlTi are compared in connection with those of B2 aluminides (FeAl, CoAl, NiAl) and titanides (FeTi, CoTi, NiTi). Thermal conductivities in three kinds of Heusler compounds $X_2YZ$ (X: Fe, Co, Ni) are almost the same value of approximately 20 Wm$^{-1}$K$^{-1}$. Ordering from B2 to L2$_1$ increases thermal conductivity in accord with the estimation by Nordheim relation. The magnitude of thermal conductivity in $X_2YZ$ Heusler compounds, including Ni$_2$GaTi, Ni$_2$AlZr and Ni$_2$AlHi, is related to those of $XY$ and $XZ$ compounds having a B2 structure.

Keywords: Heusler, intermetallic compound, thermal conductivity, periodic table, L2$_1$, B2, ordering, Nordheim rule

I. Introduction

Thermal conductivities $\lambda$ at room temperature have been reported for B2-type aluminides (FeAl, CoAl, NiAl) and titanides (FeTi, CoTi, NiTi) in the previous reports$^{(1,2)}$. For the B2 aluminides (XAl), the thermal conductivity increases with increasing the atomic number of the element X, while the opposite trend can be observed for the B2 titanides (XTi).

In Ni-Al-Ti ternary phase diagram, a Heusler-type intermetallic compound Ni$_2$AlTi ($\beta$) is obtained at the composition between B2-type NiAl ($\beta$) and NiTi ($\beta$). The Heusler alloys are a group of ternary intermetallic compounds formed at the stoichiometric composition $X_2YZ$, with the doubly ordered L2$_1$ structure based on the ordered B2, as shown in Fig. 1. Generally in most Heusler compounds $X_2YZ$, the constituent X and Y are transition metals and Z is a b-subgroup element such as Al, Si, Ga, Ge, In, Sn and Sb.

Heusler compounds, containing Mn as Y, have been well known as their ferromagnetic nature; Co$_2$MnZ$^{(3,4)}$, Ni$_2$MnZ$^{(5,6)}$, Pd$_2$MnZ$^{(7,8)}$, Au$_2$MnZ$^{(9,10)}$ and Co$_2$MnZ$^{(11,12)}$. In particular, L2$_2$ compounds are stable in the series Fe$_2$AlZ$^{(13)}$, Co$_2$AlZ$^{(14,15)}$ and Ni$_2$AlZ$^{(16,17)}$. It is attractive to make clear the order of the magnitude of the thermal conductivity in Fe$_2$AlTi, Co$_2$AlTi and Ni$_2$AlTi.

One of the purposes of this study is to clarify the effect of deviation from stoichiometry on the thermal conductivity in Ni$_2$AlTi which has a wide L2$_1$ single phase region$^{(18)}$. The other is to systematize the thermal conductivities in the large family of Heusler compounds from a viewpoint of the position of constituent elements X, Y and Z in the periodic table. Thermal conductivity in doubly ordered Heusler compound $X_2YZ$ is to be evaluated in pseudo binary system $XY$-$XZ$ for which each binary compound has ordered B2 structure.

II. Experimental

Six kinds of Heusler-type intermetallic compounds, Fe$_2$AlTi, Co$_2$AlTi, Ni$_2$AlTi, Ni$_2$GaTi, Ni$_2$AlZr and Ni$_2$AlHi are employed in this study. All specimens were produced with raw materials of high purity better than 99.9 mass% . Alloy buttons of 20 g were arc-melted on a water-cooled copper hearth under an atmosphere of purified argon. The alloy were not analyzed chemically, because the nominal composition was obtained within 0.1 mass% for the major alloying elements. The alloy buttons were sealed off in quartz tubing under a vacuum of 1 x 10$^{-4}$ Pa, followed by the homogenization at 1173 K for 86.4 ks and then water-quenched.

A disc specimen with 10 mm in diameter and 2 mm in thickness were cut off from the button ingots by electro-discharge machining. Both facets of the discs were mechanically polished to provide smooth surfaces in order to obtain parallelism for the measurement of thermal conductivity. Thermal conductivity at room temperature was measured by a laser-flash method using an ULVAC TC-7000. Details of the measurement have been described elsewhere$^{(1)}$. The accuracy of thermal conductivity in measurement were already confirmed by using pure metals and some alloys.
The L2₁ single phase is confirmed by X-ray diffraction and metallography. X-ray powder diffraction patterns were taken at room temperature by means of a JEOL diffractometer with 1 degree divergent slit. X-rays were from a CuKα target operating at 40 kV and 300 mA. A continuous scan from 20 to 120 degrees of 2θ angles with a scan speed of 1 degree per minute was taken. The resolution of the results was 0.01 degrees. An optical microscopic examination was conducted on the cutting surface of ingots after receiving heat treatment. The specimens were polished by conventional metallographic techniques using emery paper and diamond paste. The final stages of the mechanical polish were conducted using colloidal alumina. A etching procedure was employed in a solution of orthophosphoric acid saturated with chromium trioxide with a current density of 0.1 A/cm² for five minutes.

III. Results and discussion

1. X-ray diffraction

Figure 2 shows a typical example of an X-ray powder diffraction spectrum of the Heusler-type intermetallic compound, Ni₂AlTi. The spectrum obtained from L₂₁ crystal structure is divided into three categories. One is intense fundamental peaks originating from parent bcc lattice. The second is the superlattice reflection from the ordered bcc phase (B2-type). And the last one, named as super-superlattice reflection, is the evidence of the L₂₁ structure. By all these spectrum Ni₂AlTi is verified to have L₂₁ as shown in Fig. 2.

In Fe₂AlTi and Co₂AlTi having the exact integer ratio, the X-ray diffraction spectra are somewhat complicated because of the existence of the second phases. Twelve volume percent of second phase can be observed by optical microscopy in Fe₂AlTi, and four percent in Co₂AlTi at those compositions. A single phase with L₂₁ structure is achieved for Fe₂AlTi only in a restricted compositional region around Fe-30at%Al-25at%Ti at 1073 K according to the ternary phase diagram[31]. As the isothermal section of the Co-Al-Ti system, on the other hand, has not been well-established except for Ti-rich corner[31], an information about the phase field for Co₂AlTi is not available.

2. Thermal conductivity in Ni₂AlTi

Figure 3 shows the compositional dependence of the thermal conductivity at room temperature of Ni₂AlTi for the nickel concentration of 48, 50 and 52 at%. The abscissa of Fig. 3 is one half of the subtracted value of titanium concentration from aluminum one. The positive sign in the abscissa means the aluminum-rich composition, while the negative sign indicates the titanium-rich one. The abscissa of zero in the 50 at%Ni curve means the stoichiometric composition.

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Fig. 1 A unit cell of Heusler type structure is also shown, which consists of three kinds of sublattice sites, α, β and γ.

Fig. 2 Typical example of an X-ray diffraction spectrum of Heusler compound. This spectrum is taken by Ni₂AlTi at stoichiometry quenched from 1273 K.
The thermal conductivity of Ni$_2$AlTi are also shown in Fig. 4 as a function of nickel concentration under a constant titanium concentration of 25, 22, 20 and 18 atomic per cent. These results are summarized in the thermal conductivity contour as is shown in Fig. 5. It can be seen that maximum value in thermal conductivity, 21.4 Wm$^{-1}$K$^{-1}$, is obtained at stoichiometry, and by the deviation from stoichiometry in any direction the thermal conductivity decreases. The gradient of the contour is steep in constant aluminum and titanium concentrations, while it is less significant in constant nickel concentration. Interestingly, the contours of the thermal conductivity and L2$_1$ phase boundary are isomorphic.

It is a natural consequence in binary intermetallic compound to state that a singular point is obtained at stoichiometry in physical properties, e.g., lattice parameter$^{32-36}$, activation energy for diffusion$^{37-38}$, electrical resistivity$^{39-44}$ and thermal conductivity$^{41-45}$. The peculiarity at stoichiometry can be observed also in the mechanical properties, e.g., yield stress$^{46-48}$ and hardness$^{49,50}$.

At present we do not have any specific theory which can explain stoichiometry to be a singular point quantitatively in thermal conductivity. The mechanism of decrease of the thermal conductivity with deviation from stoichiometry is not well clarified quantitatively, but it is clear that some types of defects, i.e., isolated point defects (substitutional defect or constitutional vacancy) and the aggregates of such point defects, cause a disruption of periodicity in a scattering of electron waves leading to a decrease in conductivities.

Fig. 3 Thermal conductivity of Ni$_2$AlTi at room temperature as a function of composition under constant nickel concentration. The abscissa is the subtracted value of titanium concentration from aluminum one.

Fig. 4 Thermal conductivity of Ni$_2$AlTi at room temperature as a function of composition under constant titanium concentration. The abscissa is a nickel concentration.

Fig. 5 A contour map showing the magnitude of thermal conductivity in Ni$_2$AlTi. The bold line indicates the single phase field of L2$_1$ crystal structure.
3. Thermal conductivity due to ordering

The thermal conductivities at the composition of exact integer ratio of Fe$_2$AlTi, Co$_2$AlTi and Ni$_2$AlTi are plotted by solid circles against the constituent $X$ in Fig. 6. The element $X$ is arranged in the order of atomic number. It is noted here that both Fe$_2$AlTi and Co$_2$AlTi are not single phases but include a second phase as mentioned in the previous section. Shown in the parenthesis is the thermal conductivity for Fe$_2$AlTi having L2$_1$ single phase at the composition of Fe-30at%Al-25at%Ti. The data of B2 aluminides (XAl) and titanides (XTi) at the stoichiometry are also reproduced in Fig. 6 by open symbols.

An effect of second phases on thermal conductivity in Heusler compounds remains unclear in both Fe$_2$AlTi and Co$_2$AlTi. But, there seems no possibility that Fe$_2$AlTi and Co$_2$AlTi at stoichiometry without second phases have high thermal conductivities, because of the low thermal conductivity of Fe$_2$AlTi at the composition of Fe-30at%Al-25at%Ti for 9.7 Wm$^{-1}$K$^{-1}$. Conclusively, Fe$_2$AlTi, Co$_2$AlTi and Ni$_2$AlTi at stoichiometry indicate almost same thermal conductivities. Opposite trend can be observed between B2 aluminides and titanides, that is, $\lambda_{[FeAl]} < \lambda_{[CoAl]} < \lambda_{[NiAl]}$ and $\lambda_{[FeTi]} > \lambda_{[CoTi]} > \lambda_{[NiTi]}$.

The thermal conductivity data in Fe$_2$AlTi, Co$_2$AlTi and Ni$_2$AlTi at exact integer ratio are summarized in Table 1 together with those of B2 aluminides and titanides. Parentheses for Fe$_2$AlTi and Co$_2$AlTi indicate a two phase alloy, while the data at Fe-30at%Al-25at%Ti with a L2$_1$ single phase is indicated by a bracket. These data are rearranged in XAl-XTi pseudo binary system as a function of Al concentration as shown in Fig. 7. Note that the thermal conductivities of the two phase alloy are excluded in this figure. The broken lines in Fig. 7 indicate the thermal conductivity of the hypothetical continuous solid solution of B2 phase in XAl-XTi system, which is obtained based on the Nordheim relation.

Nordheim originally indicated a convex parabolic relation of electrical resistivity in some metallic binary continuous solid solutions. The electrical resistivity can be converted into thermal conductivity by eq.(1) based on the Wiedemann-Franz law which suggests thermal conductivity is inversely proportional to electrical resistivity.

$$\lambda = \frac{1}{x\lambda_A + (1-x)\lambda_B + kx(1-x)}$$  \hspace{1cm} (1)

where $\lambda_A$ and $\lambda_B$ are the thermal conductivities of the components, x is solute concentration and k is a constant which depends on an alloy system. A graphical representation of thermal conductivity calculated based on eq.(1) is characterized by a U-shaped curve on a linear scale of an ordinate, x.

It is noted that thermal conductivities of Ni$_2$AlTi with L2$_1$ single phase are higher than the calculated values of B2 solid solution. This indicates that the ordering from B2 to L2$_1$ increases the thermal conductivity. As was pointed out in Fig. 3 to 5, it is, again, recognized that the reduction rate with deviation from stoichiometry in Ni$_2$AlTi is less significant in aluminum-rich side than titanium-rich side. This can be attributed to the greater thermal conductivity in NiAl.

4. Thermal conductivity and periodic table

The L2$_1$ single phase can be achieved when aluminum in Ni$_2$AlTi is replaced with gallium which belongs to the column 3b in the periodic table, the same column as aluminum. When titanium in Ni$_2$AlTi is replaced with zirconium or hafnium belonging to column 4a, the same column as titanium, one can also achieve the L2$_1$ single phase. In this section, thermal conductivities at stoichiometry in nickel based Heusler compounds Ni$_2$YZ are discussed from the viewpoint of the periodic table, and
Table 1. Thermal conductivities at room temperature of three kinds of Heusler compounds at exact integer ratio. The data of Fe₂AlTi and Co₂AlTi having second phases are indicated in the parentheses.

<table>
<thead>
<tr>
<th>Element X</th>
<th>B2</th>
<th>L₂₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>12</td>
<td>73</td>
</tr>
<tr>
<td>Co</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>Ni</td>
<td>92</td>
<td>15</td>
</tr>
</tbody>
</table>

Fig. 8 Thermal conductivity at stoichiometry of Heusler compounds (Ni₂YTi) against the element Y at room temperature, where the constituent Y is aluminum and gallium, both of them belong to the column 3b in the periodic table.

The magnitude are evaluated with respect to the NiY-NiZ hypothetical continuous solid solution of B2 phase.

Figure 8 shows the thermal conductivity at stoichiometry as a function of the constituent Y in Ni₂YTi, where Y is either aluminum or gallium. The thermal conductivity decreases when the position of the constituent Y goes down in the periodic table in a column 3b; \( \lambda[\text{Ni₂AlTi}] > \lambda[\text{Ni₂GaTi}] \). This inequality is similar to the case of nickel based B2 compounds, \( \lambda[\text{NiAl}] > \lambda[\text{NiGa}] \) as was reported in the pervious paper(1).

The thermal conductivity data of Ni₂GaTi and NiGa are plotted for the NiTi-NiGa pseudo binary system in Fig. 9. The former data are indicated by solid while the latter ones by open triangle symbols, respectively. The thermal conductivity change of hypothetical continuous solid solution of B2 phase estimated by Nordheim relation is drawn in NiTi-NiGa system. The same analysis for NiTi-NiAl is also represented by a thin line. It is noted that the value of B2 solid solution can not be strictly estimated in NiTi-NiGa system, because no data are available for B2 solid solutions. The B2 single phase field remains unknown in this system(56). It is undoubted, however, that the magnitude of thermal conductivity in NiTi-NiGa hypothetical B2 solid solution is lower than that in NiTi-

NiAl one at any aluminum or gallium concentration. This is because of the much higher thermal conductivity in NiAl of 92 Wm⁻¹K⁻¹ as compared with 23 Wm⁻¹K⁻¹ of NiGa. The inequality in Heusler compounds, \( \lambda[\text{Ni₂AlTi}] > \lambda[\text{Ni₂GaTi}] \), would be ascribed to that of the B2 solid solutions in the pseudo binary systems.

Figure 10 shows the thermal conductivity at stoichiometry as a function of the constituent Z in Ni₂AlZ, where Z is titanium, zirconium and hafnium. The thermal conductivity scarcely decreases when the position of constituent Z goes down in the periodic table in a fixed column of 4a, which is in marked contrast to Ni₂YTi. The thermal conductivities of Ni₂AlTi, Ni₂AlZr and Ni₂AlHf are summarized in Table 2 together with those of NiTi, NiZr and NiHf. It should be mentioned that NiZr and NiHf are Daltonite compounds having the orthorhombic 3Cr-B type structure (B₂ structure)(57). If the thermal conductivity in B₂ structure does not deviate from the one for B2 structure, the thermal conductivity of hypothetical continuous solid solution of B2 phase would be almost same among the three kinds of pseudo binary systems; NiAl-NiTi, NiAl-NiZr and NiAl-NiHf. Conclusively, thermal conductivity in Heusler compound X₂YZ can be estimated from the data of B2 compounds XY and XZ.

Table 2. Thermal conductivities at room temperature of three kinds of Heusler compounds at stoichiometry. The data of NiZ are also presented. NiZr and NiHf have B₂ structure, and the value of them are indicated in the parentheses.

<table>
<thead>
<tr>
<th>Element Z</th>
<th>B₂,B₂₀</th>
<th>L₂₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>15</td>
<td>21.5</td>
</tr>
<tr>
<td>Zr</td>
<td>(23.7)</td>
<td>18.0</td>
</tr>
<tr>
<td>Hf</td>
<td>(21.3)</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Fig. 9 Nordheim relation of thermal conductivity in NiTi-NiGa pseudo binary system. The result of NiTi-NiAl is also represented. The data of Ni₂AlTi and Ni₂GaTi are indicated by solid symbols.
Fig. 10 Thermal conductivity at stoichiometry of Heusler alloys (Ni_{2}AlZ) against the element Z at room temperature, where the constituent Z is titanium, zirconium and hafnium, all of them belong to the column 4a in the periodic table.

IV. Conclusions

Thermal conductivity in Heusler-type intermetallic compounds having L2_1 structure has been investigated at room temperature using a laser-flash method. The results are summarized below.

1) In Ni_{2}AlTi, having a wide single phase field, maximum value in thermal conductivity is obtained at stoichiometry of 21.4 Wm^{-1}K^{-1}, and the deviation from stoichiometry simply reduces the conductivity in every compositional direction. The gradient is steeper in constant aluminum and titanium concentration.

2) Ordering from B2 to L2_1 increases the thermal conductivity. The increase can be estimated by the extension of the Nordheim relation to a continuous solid solution of B2 phase. The thermal conductivities in Heusler compounds Fe_{2}AlTi, Co_{2}AlTi and Ni_{2}AlTi are approximately 20 Wm^{-1}K^{-1}, which is fairly lower than those of FeTi and NiAl having B2 structure.

3) Thermal conductivities in Ni_{2}GaTi, Ni_{2}AlZ and Ni_{2}AlHF are discussed with reference to those of the continuous B2 solid solutions of NiGa-NiTi, NiAl-NiZr and NiAl-NiHf. Thermal conductivity in Heusler compound Z_{2}YZ is estimated from the data of XY and XZ without any experiment, if XY and XZ have B2 structure.

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