1 Introduction
Fiber Reinforced Polymer (FRP) has excellent mechanical characteristics, such as lightness and high strength. Therefore, it has been extensively investigated as an alternative material to metals, and recently, it has been used as the structural material of aircraft, spacecraft, and hydrogen pressure vessels for automobiles. In addition to such excellent properties, FRP has much lower thermal conductivity than metals and is used as structural material in cryogenic engineering. In designing cryogenic apparatus such as liquid hydrogen tanks, both strength design and thermal design are important to reduce the amount of heat flow from the surroundings.
Kamiya et al. [1] studied a conceptual design of a large liquid hydrogen (LH2) storage tank. They adopted Glass Fiber Reinforced Polymer (GFRP) for supports connecting the cryogenic tank and an outer chamber at room temperature. They also proposed a thermal insulation structure of large LH2 tank, but could not show the performance of the tank due to a lack of thermal conductivity data of GFRPs. Tsubaki [2] also studied insulation structures of a LH2 tank of 10,000 m³ and proposed the optimum insulation structure using GFRP to achieve the boil-off rate of 0.16 wt% per day. However, because the rate is strongly affected by the thermal conductivity of GFRP, its accurate values from a room temperature to about 20 K are required for the evaluation of the boil-off rate.
Thermal conductivity of FRP will be affected by factors such as fiber material, matrix, fiber direction, fiber content, and so on. Reed et al. [3] have reviewed the mechanical and thermal properties of unidirectional composites with glass, carbon, boron, alumina, and aramid fibers at cryogenic temperature. Based on the ratio of strength to thermal conductivity, they concluded that GFRP is the best support material among the FRPs above 20K. Kasen [4] reviewed many works of research on the mechanical and thermal properties of GFRPs at cryogenic temperatures. He revealed discrepancies among the thermal conductivity data obtained by some researchers, and pointed out that one of the causes of the discrepancies may be inaccuracy of their experiments. In addition, Radcliffe et al. [5] studied effects of fiber-direction and fiber-content of GFRPs and carbon FRPs (CFRPs) on the thermal conductivity from 2 to 80 K. The thermal conductivity parallel to the fiber was 10-20% higher than that perpendicular to the fiber and both were proportional to fiber-content. Dmitrevsky et al. [6] measured thermal conductivities of glass-fabric-base laminates and uniaxial-glass-fiber-base laminates in the temperature range of 4 to 80K, and obtained trends similar to Radcliffe’s results. The matrices they adopted were different but the both have almost the same thermal conductivities and the fibers they adopted were E-glass. Therefore, although it was assumed that thermal conductivities of their unidirectional GFRPs should show almost the same values, they did not agree well. This result suggests that we should measure thermal conductivity with higher accuracy under cryogenic condition. However, in most of the literature mentioned previously [3-6], measurement accuracies were not discussed enough.
In the previous study [7], Tanaka analyzed errors in measuring temperature after reducing the amount of heat flow by convection and radiation, and pointed out that we should consider heat flow through the thermocouple wire. He tried to reduce thermal contact resistance (TCR) between the thermocouple and the specimen by improving contact conditions but failed to reduce it to a negligible value. In this research, a temperature compensation method using TCR between the specimen and the thermocouple was proposed [8] and the thermal conductivity of GFRP was actually measured between 20 and 80 K.
2 Temperature Compensation with Thermal Contact Resistance

In cryogenic experiments, heat flow from the surroundings to the specimen should be reduced enough. In general, the specimen is covered by radiation shields and experiments are performed under vacuum condition. If proper countermeasures are taken, the amount of heat flow by those heat transfers will be in negligible levels. However conduction through a conductive wire of the temperature sensor still remains as a possible heat flow mechanism.

A Silicon diode thermometer (SD thermometer) and a ruthenium oxide resistant thermometer (RuO thermometer) are commonly used as cryogenic temperature sensor. If we use a manganin wire as the conductive sensor wire, because its thermal conductivity is low enough, heat flow through the conductive wires can be negligible. But their sensor heads are not small enough for the measurements of local temperatures. An Au(0.07%Fe)/chromel thermocouple (AF thermocouple) is also commonly used as a thermocouple for cryogenic temperature range. As it has a tiny sensor head, it is very suited for a measurement of a temperature distribution in a specimen. However, as an Au(0.07%Fe) wire has large thermal conductivity, we must take a proper countermeasure for temperature measurement.

Generally, there is TCR between two solid surfaces. In a room temperature range, the resistance is usually small enough. But in cryogenic temperatures, it is not ignorable in many cases, because the temperature difference between the specimen and the thermocouple based on the TCR becomes a comparable value with the temperature measured. To improve the contact condition, we usually apply a load and make the resistance small enough. Figure 1 shows a schematic image of a thermocouple inserted into a specimen. It is obvious from this figure that we cannot apply a load between the specimen and the thermocouple inserted into a hole, and therefore the TCR cannot be negligible.

By considering the situation previously mentioned, we change our way of thinking from reduction of the TCR to acceptance of the resistance. Here, we propose to compensate temperatures measured with thermocouples by a temperature gap based on the TCR. Equation 1 shows the relationship between the specimen temperature, T_S, and the thermocouple temperature, T_TC. In order to use this compensation method, we must know the TCR, R, in advance and control the heat flow through the thermocouple into the specimen, \( \dot{Q}_{\text{con}} \).

\[
T_S = T_{TC} - R\dot{Q}_{\text{con}} \tag{1}
\]

3 Experimental

3.1 GFRP Specimens

In this experiment, GFRP having the lowest thermal conductivity among FRPs above 20 K [3], was used in the thermal conductivity measurements under the cryogenic region. First, a unidirectional GFRP block was prepared by the hand lay-up method with laminated prepreg-sheets of 46% fiber-content (GE 352H160S, Mitsubishi Rayon Co., Ltd.). Secondly, a load was applied to the GFRP block by clamping it with copper plates, and it was sintered in a thermostatic bath at 130 °C. Finally, two pairs of pieces were cut out of the GFRP block. Each pair had the same fiber orientation, but consisted of two pieces of different lengths (30 mm as group “A” and 10 mm as group “B”). Two specimens with a fiber orientation of 0 degree to its longitudinal direction were called A0 and B0. Similarly, the other two with a fiber orientation of 90 degree were called A90 and B90 (see Fig. 2). The cross-sectional area of the specimens was 14 mm².

![Fig. 1. Schematic image of temperature measurement point.](image)

![Fig. 2. CFRP specimens (Top view).](image)
For the specimens A0 and A90, three holes of 1 mm diameter were drilled to the center of specimen at 7.5 mm intervals. In addition, bisphenol-A epoxy resin, which is the same resin as the prepreg-sheets, was poured into the holes. Then three calibrated AF-thermocouples (TC1, TC2, and TC3) were inserted into the holes, and it was left at room temperature until the resin cured. After curing, the TCRs between each thermocouple and the specimen were expected to be constant, but not necessarily equal. For the specimens B0 and B90, a hole of 2 mm diameter was drilled to the center of each specimen, and a SD thermometer was inserted into the hole with cryogenic grease (Apiezon-N grease).

### 3.2 Thermal Contact Resistance Measurement

In order to measure the thermal contact resistance, which is usually unknown, we developed a new experimental system shown in Fig. 3. The specimens A and B, having the same fiber direction, are sandwiched tightly with aluminum plates. The assembly was attached to a cold stage in a cryostat to establish a uniform temperature field on the test section. The pressure in the cryostat was kept at about 1.3×10³ Pa. In addition, as the manganin conductive wires for the SD thermometer were attached to the aluminum plates, the SD thermometer could accurately indicate the specimen temperature. On the other hand, due to the TCR and heat flow through the thermocouple, a temperature difference between the specimen and the thermocouple occurred. The amount of heat flow, \( \dot{Q}_{\text{con}} \), through the thermo-couple was controlled with varying the thermal anchor temperature. It was assumed that the heat flow only occurred through the Au (0.07%Fe) wire, and it can be obtained from solving Equation 2.

\[
\dot{Q}_{\text{con}} = \frac{S}{L} \int_{T_{TC}}^{T_{TA}} \lambda_{\text{Au}} dT
\]

Here, \( \lambda_{\text{Au}} \) is thermal conductivity of Au [9], \( T_{TC} \) is the measured temperature of the thermocouple, \( T_{TA} \) is the temperature of the thermal-anchor, \( S \) is the cross sectional area of Au wire, and \( L \) is the wire length between specimen and thermal anchor. Once the value of \( \dot{Q}_{\text{con}} \) is obtained by solving Equation 2, the TCR can be determined by Equation 1.

### 3.3 Thermal Conductivity Measurement

Using the temperature compensation, the thermal conductivities of the GFRP specimens (A0 and A90) mentioned previously were measured with the one dimensional steady state method.

\[
\dot{q} = \frac{\dot{Q}}{A} = \frac{dT}{dx}
\]

Figure 4 shows the schematics of the test section. The cold stage and a heater were attached to the specimen. In order to improve the contact conditions of the specimen, silver paste was used in between the cold stage and the specimen and Apiezon-N grease in between the specimen and the heater. The specimen was insulated by an aluminum radiation shield under vacuum condition, and then the heat transfer by radiation and convection became negligible.

The specimen temperature was controlled by changing the cold stage temperature from 20 to 80 K. The heater output was in between 15 and 30 mW. The thermal anchor was common to all thermocouples measuring the temperatures at the different points of the specimen and its temperature was set higher than the specimen temperatures. The amount of heat input through each thermocouple was in between 0.5 and 1.5 mW. Two of the three...
thermocouples were selected to estimate the thermal conductivity with Equation 3. Here, the heat flow rate, $\dot{Q}$, was considered as the summation of the heat flows from the heater and through each thermocouple.

4 Results and Discussions

4.1 Thermal Contact Resistance

Thermal contact resistances of the specimens A0 and A90 were measured in the temperature range from 20 to 80 K. The temperatures of specimens B0 and B90, which were measured by the SD thermometer, matched the cold stage temperature. Thus, the uniform temperature field could be established on the test section. Therefore, we assume that the SD thermometer indicates the temperatures of specimens A0 and A90. Figure 5 shows the temperature differences, $T_{TC} - T_s$, with respect to the amount of the heat flow through the thermocouples, $\dot{Q}_{con}$. The data seemed to be scattered as a whole, and maximum temperature difference was about 5 K. However, the straight lines fitting of each data set could be distinguished as a line from the origin or not. The data of TC1 and TC3 for A90 could be approximated as the lines from the origin, and those results indicated that TCR is constant and independent of temperature. On the other hand, the TC2 data for A90 and the data of all the thermocouples for A0 could not be approximated as lines from the origin. From the results, we consider two possibilities. The first is that the TCR in Equation 1 will change with temperature. The other is that the TCR is constant but the contact condition will change with the temperature. Near room temperature TCR is generally considered constant but there may be a possibility that TCR will change with temperature in low temperature region. In order to examine the temperature dependency, the data of TC1 for A0 were divided into temperature ranges of $T_{TC}$ by every 10 K as shown in Fig. 6. The slopes of the fitting lines seem to be almost the same for all the temperature ranges, and the y-intercepts increase as the temperature decreases. Considering the results, we adopt Equation 4 instead of Equation 1. The average value of the slopes can be considered as $R$ in the equation. We don’t know whether we should call the whole of these terms as TCR or not, but for convenience, hereafter, we will refer to this $R$ as TCR.

![Fig. 5](image1)

(a) Fiber direction: 0 degree (A0)

![Fig. 6](image2)

(b) Fiber direction: 90 degree (A90)

Fig. 5. Temperature difference, $T_{TC} - T_s$, versus heat flow rate through thermocouple, $\dot{Q}_{con}$.

Fig. 6. Temperature difference, $T_{TC} - T_s$, for each temperature range (A0, TC1).
\[ T_S = T_{TC} - \{ R \dot{Q}_{con} + f(T) \} \] (4)

Next, we investigated the form of \( f(T) \). Figure 7 clearly shows it can be expressed as a linear equation of thermocouple temperature, \( T_{TC} \). Then, Equation 4 can be rewritten as Equation 5.

\[ T_S = T_{TC} - \{ R \dot{Q}_{con} + (C_1 T_{TC} + C_2) \} \] (5)

Here, the constants, \( C_1 \) and \( C_2 \), were determined by the least-square method. To confirm consistency of this procedure, we rearranged the data by subtracting this term from the temperature difference, \( T_{TC} - T_S \). Figure 8 shows the scattered data was well rearranged and could be expressed by a linear equation from the origin. The slope of this line, \( R' \), should correspond to the TCR. Table 1 shows the values of \( R, C_1, C_2, \) and \( R' \) for each thermocouple. As the values of \( R \) and \( R' \) agree well, we think this procedure is reasonable.

In order to study the causes of the temperature-dependent term, we observed the cross sections of the specimen with a scanning electron microscope. Figure 9 shows the cross sections of the specimens around the junctions of thermocouples. In the photos of TC1 and TC3 for A90, we observed a void or a crack around the thermocouples. But in the others we couldn’t recognize them clearly. Of course, from these photos, it may be very hard to say that the cause is contact conditions between the specimen and thermocouples. But it might be necessary to study an effect of thermal stress on thermoelectromotive force.

We estimated the maximum errors, \( \Delta T_{\text{max}} \), and the mean square deviations, \( \Delta T_{\text{rms}} \), of all the data after the compensation for each thermocouple by Equations 6 and 7. In the equations, \( T_S \) is the specimen temperature and \( T_S^* \) is the compensated temperature of thermocouple. The results for each thermocouple were shown in Table 2. By this compensation method, the maximum errors were

\[ \Delta T_{\text{max}} = \max \left| T_S^* - T_S \right| \] (6)

**Fig. 7. Temperature-dependent term (A0, TC1).**

**Fig. 8. Thermal contact resistance (A0, TC1).**

**Table 1. Constants in Equation 5.**

<table>
<thead>
<tr>
<th></th>
<th>( R ) [K/mW]</th>
<th>( C_1 ) [K/K]</th>
<th>( C_2 ) [K]</th>
<th>( R' ) [K/mW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>TC1 0.267</td>
<td>-0.0369</td>
<td>4.327</td>
<td>0.264</td>
</tr>
<tr>
<td></td>
<td>TC2 0.315</td>
<td>-0.0200</td>
<td>2.646</td>
<td>0.315</td>
</tr>
<tr>
<td></td>
<td>TC3 0.194</td>
<td>-0.0235</td>
<td>2.975</td>
<td>0.191</td>
</tr>
<tr>
<td>A90</td>
<td>TC1 0.641</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>TC2 0.750</td>
<td>-0.0309</td>
<td>2.959</td>
<td>0.751</td>
</tr>
<tr>
<td></td>
<td>TC3 1.293</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Fig. 9. SEM images of the cross sections of GFRP specimens around temperature measurement points.**
\[ \Delta T_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (T_{S_i}^* - T_{S_i})^2} \]  

(7)

Reduced from 5 K to less than 0.7 K and the mean square deviations were about 0.3 K. Therefore, we can conclude the temperature compensation method proposed is effective to improve temperature measurement at low temperatures.

### 4.2 Thermal Conductivity

Figures 10 and 11 show the thermal conductivities of the specimens A90 and A0, without and with the temperature compensation in the cryogenic temperature region. In the figures, three thermal conductivities are shown according to a pair of the thermocouples. The subscript of each \( \lambda \) represent a pair of the thermocouples selected for the calculation. In addition, the total errors of \( \lambda_{13} \) at about 70 K is shown in the figures. Although the three thermal conductivities for the specimen should agree, those for A90 without temperature compensation showed unignorable differences, but those obtained with the compensation agree well (Fig. 10). On the other hand, with compensation, the conductivities are in good agreement and show the expected behavior.

<table>
<thead>
<tr>
<th>[K]</th>
<th>A0</th>
<th></th>
<th>A90</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TC1</td>
<td>0.35</td>
<td>0.35</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>TC2</td>
<td>0.54</td>
<td>0.54</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>TC3</td>
<td>0.47</td>
<td>0.47</td>
<td>0.68</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 2. Errors of temperature measurement with the compensation.

**Fig. 10.** Thermal conductivities perpendicular to the fiber direction (A90).

**Fig. 11.** Thermal conductivities parallel to the fiber direction (A0).
hand, differences among the three thermal conductivities of the specimen A0, were fairly small regardless of the compensation, the total measurement error was reduced so much by the compensation (Fig. 11). Anyway, the thermal conductivities of the GFRP increase from 0.1 to 0.3 W/(m·K) with the temperature from 20 to 80 K.

The total error of the thermal conductivity measurement is composed of temperature measurement error, length measurement error, and error of the heat flow rate in the specimen. As the effects of the radiation and the heat conduction can be considered negligible, the error of the heat flow rate is also negligible small. The length measurement error seems to be mainly caused by a thermal shrinkage of the specimen and the most important factor is the temperature measurement error. The error of the temperature measurement, \( \Delta T \), with the temperature compensation is \( \Delta T_{\text{ms}} \) mentioned previously. On the other hand, \( \Delta T \) without the compensation is assumed as the mean temperature error in the range where \( Q_{\text{con}} \) is smaller than 1.5 mW in Fig. 5, because 1.5 mW is the maximum heat input through the thermocouple. The total error of the thermal shrinkage is simplified as a sum of the shrinkage of the triaxial components of the matrix from the room temperature to the working temperature [10]. The error of each factor and the total errors of \( \lambda_{13} \) is shown in Table 3. Here, \( \Delta \lambda_{13}/\lambda_{13} \) is the total error of \( \lambda_{13} \), \( Q \) is the heat flow rate in the specimen. The maximum total error of \( \lambda_{13} \) can be reduced from about 60\% to 15\%. Those of both \( \lambda_{12} \) and \( \lambda_{13} \) with the compensation become about 25\%. Then, effect of the fiber direction on the thermal conductivity of GFRP specimens was investigated.

As \( \lambda_{13} \) was the most accurate, it was used in the following discussion. Figure 12 shows the thermal conductivities, \( \lambda_{13} \), of A0 and A90 and the thermal conductivity parallel to the fiber, A0, is 10\% larger than that perpendicular to the fiber, A90. In the previous studies, measurement accuracy was insufficient to study the effect, but as the temperature compensation method improved it significantly, we could show the effect clearly.

Some models for estimating thermal conductivities of composites material have been proposed. Equation 8 is a typical equation for the thermal conductivity parallel to the fiber (Parallel model), and Equation 9 for that perpendicular to the fiber (Rayleigh model [11]).

\[
\lambda = V_f \lambda_f + (1-V_f) \lambda_m
\]

\[
\lambda = \lambda_m \left( 1 - \frac{2V_f}{V_f + \frac{3V_f^4}{\pi^2} (0.032\pi^4)^2} \right)
\]

In these equations, \( \lambda_f \) is the thermal conductivity of the fibers, \( \lambda_m \) is the thermal conductivity of the matrix, \( V_f \) is the volume content of the fibers, and \( v \) is a coefficient defined by the thermal conductivities of the fiber and matrix ( \( v = (\lambda_m + \lambda_f)/(\lambda_f + \lambda_m) \) ). Figure 13 shows a comparison of the measured and the estimated thermal conductivities. The measured thermal conductivities were the same in Figure 12. In the estimation, \( V_f = 0.46 \) was assumed and the thermal conductivities of E-glass by Radcliffe [5] and epoxy resin in the Reference 12 were used. The estimated values of the thermal conductivities for A0 and A90 don’t agree with the measured values. On the other hand, Domitrevsky reported a different value for glass fiber. Although the fibers in the prepreg-sheets we used are E-glass, there might be

<table>
<thead>
<tr>
<th>( Q ) [mW]</th>
<th>Temp. compensation</th>
<th>( T ) [K]</th>
<th>( \Delta T_{\text{TC1}} ) [K]</th>
<th>( \Delta T_{\text{TC3}} ) [K]</th>
<th>( \frac{\Delta T_{\text{TC1}}}{T_{\text{TC1}} + T_{\text{TC3}}} \times 100 ) [%]</th>
<th>( \frac{\Delta T_{\text{TC3}}}{T_{\text{TC1}} + T_{\text{TC3}}} \times 100 ) [%]</th>
<th>Thermal shrinkage (total) [%]</th>
<th>( \Delta \lambda_{13} / \lambda_{13} ) [%]</th>
<th>Total error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0 &amp; 15</td>
<td>without &amp; 20-40</td>
<td>2.22</td>
<td>1.62</td>
<td>23.0-32.3</td>
<td>16.8-23.5</td>
<td>4.1</td>
<td>44-61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; with &amp; 20-40</td>
<td>0.20</td>
<td>0.22</td>
<td>2.9-4.1</td>
<td>3.2-4.5</td>
<td>4.1</td>
<td>10-14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; with &amp; 30-85</td>
<td>0.20</td>
<td>0.22</td>
<td>1.8-3.2</td>
<td>2.0-3.6</td>
<td>4.1</td>
<td>8-13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A90 &amp; 15</td>
<td>without &amp; 30-65</td>
<td>0.60</td>
<td>1.13</td>
<td>7.2-11.7</td>
<td>13.5-22.0</td>
<td>4.1</td>
<td>32-39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; with &amp; 30-65</td>
<td>0.31</td>
<td>0.23</td>
<td>3.0-4.8</td>
<td>2.2-3.6</td>
<td>4.1</td>
<td>10-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; without &amp; 40-100</td>
<td>0.60</td>
<td>1.13</td>
<td>4.5-8.0</td>
<td>8.5-15.0</td>
<td>4.1</td>
<td>18-30</td>
<td></td>
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<tr>
<td>&amp; with &amp; 40-100</td>
<td>0.31</td>
<td>0.23</td>
<td>2.0-4.0</td>
<td>1.5-3.0</td>
<td>4.1</td>
<td>8-14</td>
<td></td>
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</tr>
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</table>
some possibilities that the thermal conductivity of the fibers have different value, because of the composition and the crystallinity degree. For further discussions on a validity of those estimation methods, we need to know the accurate value of the thermal conductivity of glass fiber in GFRP.

5 Conclusion
A temperature compensation method based on the thermal contact resistance between the specimen and a thermocouple was proposed. The TCR between a GFRP specimen and an AF thermocouple was measured. Thermal conductivities of GFRP were measured in the temperature range from 20 to 80 K and are 0.1-0.3 W/(m·K). Effect of the fiber-direction is clearly shown that thermal conductivity of GFRP for 0 degree is about 10% larger than that for 90 degree.
With the temperature compensation, the maximum temperature measurement errors could be reduced from 5 K to 0.7 K, and the mean-square-deviations of the error was 0.3 K.

Reference