Development of Fe-based superconducting wires for liquid-hydrogen level sensors

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Abstract. We developed liquid-hydrogen (LH₂) level sensors with Ba(Fe₁₋ₓCoₓ)₂As₂ superconducting wires (Co-Ba122 wires) as their detection elements. We fabricated Co-Ba122 wires with different Co concentrations x by using the powder-in-tube method. The superconducting transition temperatures of the wires were successfully controlled in the range of 20–25 K by changing x from 0.06 to 0.10. The resistance–temperature curves of the wires exhibited sharp superconducting transitions with widths of 0.5–1.0 K. In addition, we performed an operation test of the Co-Ba122 level sensors with LH₂. Close correspondence between the output resistance and the actual LH₂ level was observed for a sensor equipped with x = 0.09 wire, demonstrating that this sensor can accurately measure LH₂ levels.

1. Introduction

Hydrogen is a potential source of clean energy whose liquid form is advantageous for transportation and storage due to its high density. To ensure the safety of these processes, accurate monitoring of the liquid hydrogen (LH₂) levels in tanks is required. Superconducting wires can be used as the detection elements of LH₂ level sensors because their output resistances are sensitive to the LH₂ level. For superconducting wires composed of a given material to be usable in LH₂ level sensors, the superconducting transition temperature (Tc) must be higher than the boiling point of LH₂ (TlLH₂ ~ 20.3 K at atmospheric pressure). In the LH₂ level sensors developed so far, MgB₂ superconducting wires with Tc = 30–35 K have been used as the detection elements [1–3]. However, those LH₂ level sensors require heating systems to improve their level detection accuracies because the value of Tc for MgB₂ is rather high compared with TlLH₂; thus, MgB₂ wires become superconducting even at temperatures at which hydrogen is in its gaseous form (GH₂). Accordingly, superconducting materials with Tc values close to TlLH₂ are considered to be good candidates for the materials of the wires used as the detection elements of LH₂ level sensors.

Iron-based superconductors [4] have attracted significant attention due to their high Tc values and high upper critical fields, which are suitable for high-field applications. To evaluate the practical application potential of such superconductors, iron-based superconducting wires and tapes have been developed to achieve high critical currents in high magnetic fields [5–7]. Iron-based superconductors are also advantageous for use in sensor applications due to their wide variety of Tc values. Here, we focus on an iron-based superconductor, Ba(Fe₁₋ₓCoₓ)₂As₂ (Co-Ba122) [8], as a candidate material for the detection elements of LH₂ level sensors. Co-Ba122 possesses a maximum Tc of 25 K, and Tc can be tuned by varying the Co concentration x [9,10]. Since Tc can be adjusted until it is close to TlLH₂, it is...
interesting to examine the feasibility of using Co-Ba122 wires as the detection elements of LH2 level sensors.

In this study, we fabricated Co-Ba122 superconducting wires with different x by using the powder-in-tube method. We successfully controlled the $T_c$ values of the wires in the range of 20–25 K by varying $x$ from 0.06 to 0.10. The superconducting transitions in the resistance–temperature curves were quite sharp, with widths of 0.5–1.0 K. We then developed LH2 level sensors based on the Co-Ba122 wires and performed an operation test with LH2. The output resistances and actual LH2 levels corresponded closely with one another, demonstrating that the level measurements were highly accurate [11].

2. Experimental

2.1. Fabrication of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconducting wires

Polycrystalline powders of Co-Ba122 ($x = 0.06–0.10$) were synthesized via a solid-state reaction. Before synthesizing the polycrystalline samples, BaAs, Fe$_2$As, and Co$_2$As were prepared as precursors. The starting materials (Ba (3N, chunks), Fe (4N, 150 $\mu$m mesh), Co (4N, 150 $\mu$m mesh), and As (6N, 1-5 mm grains)) were weighed and heated for 10 h at 650 °C (BaAs) and 850 °C (Fe$_2$As and Co$_2$As). The precursors were weighed and mixed with a ratio of BaAs : Fe$_2$As : Co$_2$As = 1 : 1 - $x$ : $x$. The mixture was sealed in a quartz tube and heated at 900 °C for 48 h. All of the materials were handled in a nitrogen-filled glove box.

The Co-Ba122 superconducting wires were fabricated by using the ex-situ powder-in-tube method. The polycrystalline bulks were ground into powders with an agate mortar in a glove box. The powders were filled into a silver tube with outer and inner diameters of 6 mm and 4.3 mm, respectively. The silver tube was groove-rolled into a square wire with a 1.2 $\times$ 1.2 mm$^2$ cross-section. The wires were cut into 4-cm- and 20-cm-long pieces, sealed into a quartz tube, and heated at 880 °C for 20 h. An example scanning electron microscope (SEM, Hitachi High-Technologies TM3000) image of the transverse cross-section is presented in Figure 1(a). The resistances of the short wires were measured by using a four-probe method, and the contacts were made of solder.

Figure 1. (a) SEM image of the transverse cross-section of a Co-Ba122 wire. The gray and silver regions correspond to the superconducting core and silver sheath, respectively. Photographs of (b) a 20-cm-long Co-Ba122 wire and (c) an assembled level sensor.
2.2. Development of the liquid hydrogen level sensors and operation test

Figures 1(b) and 1(c) present photographs of a 20-cm-long Co-Ba122 wire used for the LH$_2$ level sensor and an assembled level sensor, respectively. The contacts were formed by soldering and were separated by 175 mm. The wires were placed into straws, which were used as protecting tubes.

Figure 2(a) shows a photograph of the setup used in the operation test. The LH$_2$ level sensor was installed in the cryostat with observation slits. The LH$_2$ was prepared using the hydrogen liquefier [12]. It was transferred from the liquefier to the cryostat through a transfer tube. Figure 2(b) is a schematic of the experimental setup, which consisted of a Co-Ba122 level sensor, current source (denoted as $I$ in Figure 2(b)), voltmeter ($V$), and personal computer (PC). The output resistance of each sensor was measured by using a four-probe method. The actual LH$_2$ level was checked by reading a scale attached to the level sensor. The output resistance and actual LH$_2$ level were recorded every 5 min during the natural evaporation of the LH$_2$.

![Figure 2. (a) Photograph and (b) schematic of the experimental setup used in the operation test.](image)

3. Results and discussion

3.1. Characterization of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconducting wires

Figure 3(a) depicts the temperature ($T$) dependences of the resistances ($R$) of 4-cm-long Co-Ba122 wires with $x = 0.06$, 0.07, 0.08, 0.09, and 0.10. A relatively small current of 10 mA was applied to perform the measurements. For each of the wires, a large drop in $R$ corresponding to the superconducting transition is observable. This large drop is necessary to obtain a high signal-to-noise ratio without applying a large current. The normal-state $R$ of each wire exhibits a weak $T$ dependence characterized by a ratio of $R(300 \text{ K})/R(30 \text{ K}) = 1.3–1.5$. The weak $T$ dependence is advantageous because it results in the output $R$ of the wires not being affected significantly by the gradient or variations of $T$ in GH$_2$. Figure 3(b) shows a magnified section of the $R$–$T$ curves around $T_c$. The superconducting transitions of the wires are very sharp with the widths $\Delta T_c$ of 0.5–1.0 K, except in the case of $x = 0.06$ ($\Delta T_c$ was determined by the difference between the values of $T$ corresponding to $R$ values equal to 5% and 95% of the normal-state $R$). A sharp transition is also essential to achieve high-resolution liquid level detection. The broad transition exhibited by the $x = 0.06$ wire is a result of the existence of the antiferromagnetic–orthorhombic phase on the underdoping side of the superconducting dome, where slight inhomogeneities in the Co atom distribution cause significant spatial variation of $T_c$. Figure 3(b) confirms that $T_c$ varies systematically with $x$ for the Co-Ba122 wires; the $T_c$ values determined based on
the values of $T$ at which $R = 0 \, \text{m}\Omega$ were found to be 16.3 K, 24.1 K, 23.4 K, 21.8 K, and 20.1 K for $x = 0.06$, 0.07, 0.08, 0.09, and 0.10, respectively. The $x$ dependence of $T_c$ is summarized in the inset of Figure 3(b). These results illustrate that $T_c$ can be controlled in Co-Ba122 by adjusting $x$. The $x = 0.06$ and 0.10 wires with $T_c$ lower than $T_{LH2}$ are not available because $R > 0$ at $T = T_{LH2}$. Among the investigated wires, the $x = 0.09$ wire, for which $T_c$ is 1.5 K higher than $T_{LH2}$, is expected to be most suitable for use in LH$_2$ level sensors.

![Figure 3](image-url)  

**Figure 3.** (a) $T$ dependence of $R$ for Co-Ba122 wires with $x = 0.06$, 0.07, 0.08, 0.09, and 0.10. (b) Magnified section of the $R$–$T$ curves around $T_c$. The inset shows the $x$ dependence of $T_c$. The dashed line indicates $T_{LH2} (= 20.3 \, \text{K})$.

### 3.2. Operation test of level sensors with liquid hydrogen

We assembled level sensors using the Co-Ba122 wires discussed in Section 3.1 and performed an operation test with LH$_2$. The sensors equipped with $x = 0.07$ and 0.09 wires ($T_c = 24.1 \, \text{K}$ and 21.8 K) were labelled as Sensors A and B, respectively. Figure 4(a) shows the time ($t$) dependences of the LH$_2$ level (blue) and output $R$ of Sensors A (black) and B (red). For an LH$_2$ level of 180 mm (at which point we defined $t$ to be 0 min), which was 5 mm above the upper voltage contacts of the sensors, both sensors exhibit $R = 0 \, \text{m}\Omega$. Sensor A shows $R = 0 \, \text{m}\Omega$ until $t \sim 30$ min, when the LH$_2$ level reaches 130 mm, i.e., 45 mm below the upper voltage contact. This finding indicates that the upper part of Sensor A, which was already in GH$_2$, remained superconducting due to the high $T_c$ of the wire used in Sensor A. For $t > 30$ min, $R$ is finite and increases with $t$ in response to the decrease of the LH$_2$ level. However, $R$ continues to increase even after the LH$_2$ level is below the lower voltage contact. These results indicate that LH$_2$ levels determined based on the output $R$ of Sensor A will be overestimates. Thus, as has been reported previously [1–3], Sensor A requires a heating system to be capable of detecting LH$_2$ levels accurately.

On the other hand, Sensor B, for which the $T_c$ of the wire is closer to $T_{LH2}$ than that of the wire in Sensor A, exhibits a finite $R$ at $t \sim 5$ min, which corresponds to an LH$_2$ level of around 170 mm, i.e., 5 mm below the upper voltage contact. This finding indicates that Sensor B responds to LH$_2$ level decreases more accurately than Sensor A does. Furthermore, $R$ is almost constant for Sensor B after the LH$_2$ level effectively reaches 0 mm. Based on the $t$ dependences of the LH$_2$ level and $R$, we plotted the LH$_2$ level against $R$ for Sensor B; the resulting graph is presented in Figure 4(b). The two quantities exhibit a strong linear correlation described by LH$_2$ level (mm) = 169.7 - 1.674$R$ (m$\Omega$) with a linear
correlation coefficient $|r|^2$ of greater than 0.99. Although Sensor B slightly overestimates the LH$_2$ level, its measurements are reasonably accurate, and it does not require a heating system. In addition, more accurate measurements could be achieved if $T_c$ were made closer to $T_{LH2}$ by refining $x$.

![Figure 4](image)

Figure 4. (a) $t$ dependences of the LH$_2$ level (blue) and output $R$ of Sensor A ($x = 0.07$ wire, black) and Sensor B ($x = 0.09$ wire, red). (b) Relationship between $R$ of Sensor B and the LH$_2$ levels derived from (a). The black solid line indicates the linear fit determined using the least-squares method. The fitting function is also provided in the panel.

4. Summary

We developed LH$_2$ level sensors with Co-Ba122 superconducting wires as their detection elements. The $T_c$ values of the wires were successfully controlled in the range of 20–25 K by varying $x$. In addition, the Co-Ba122 wires exhibited sharp superconducting transitions, and their normal-state $R$ values showed weak $T$ dependences; both of these characteristics make these wires advantageous for use in level sensors. In addition, we performed an operation test of the Co-Ba122 level sensors with LH$_2$. We demonstrated that the Co-Ba122 level sensor whose wires had $T_c$ close to $T_{LH2}$ yielded reasonably accurate level measurements without requiring a heating system. The accuracy will be further improved by fine-tuning $T_c$.

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