Optimization of loading ratio of ErN as regenerator of 4K-GM cryocooler

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Abstract. High purity erbium nitride (ErN) spheres with the size range of 150-180 μm and 180-212 μm were prepared by nitriding Er metal spheres with low oxygen content. The initial regenerator material of HoCu₂ on the cold end of the second regenerator column in 4K-GM cryocooler with nominal cooling power of 0.1 W at 4.2 K was replaced by ErN with different sizes. Higher cooling power was obtained when ErN of smaller size with lower oxygen content was used. We investigated the effect of partial replacement of HoCu₂ by ErN in the cold end side of second stage regenerator column on cooling power of 4K-GM cryocoolers. When ErN were substituted for 20 % of HoCu₂, the cooling power at 4.2 K reached 0.318 W. This value was 1.36 times as high as that of the cooling power of the GM cryocooler with commercially available regenerator arrangement. Therefore, use of ErN regenerator materials leads to the energy-saving and downsizing of 4K-GM cryocoolers.

1. Introduction

Gifford-McMahon (GM) cryocoolers are typical 4 K cryogenic refrigerators widely used for ultra high vacuum pumps, helium and hydrogen liquefaction, and for systems using superconducting magnets such as magnetic resonance imaging diagnosis devices and magnetic levitation trains. However, to obtain 1 W of cooling power at 4.2 K using GM cryocoolers, input power as much as several kW is needed. It is a very important problem to enhance their performances at cryogenic temperatures from the view of the energy saving. The 4K-GM cryocoolers have 2 stages of regenerators. By repeating compress and expansion of helium gas, cryogenic temperate is formed. The first-stage regenerator consists of stacked copper meshes, and the second consists of packed Pb and HoCu₂ spheres. The performance and efficiency of the 4K-GM cryocoolers depend on the second stage regenerator materials. The most important requirement for the regenerator materials are large specific heat around the working temperatures. To improve the efficiency, the researchers and engineers are seeking advanced regenerator materials [1-4].
We have reported rare earth nitrides (ErN, HoN, DyN, TbN and GdN) have large specific heat at cryogenic temperatures [5, 6]. Among them, ErN shows a peak of specific heat at 4 K. Thus, ErN was expected to be suitable materials for second stage regenerator of 4 K GM cryocoolers. In fact, we have prepared spherical ErN with different sizes and tried to use second stage regenerator for GM cryocooler with nominal cooling power of 0.1 W at 4.2 K [7]. We succeeded to form 4.2 K using the GM cryocooler with ErN regenerator. The cooling power of the GM cryocooler at 4.2 K became higher when the ErN spheres with smaller sizes were used. In previous works, we used Er spheres containing 1.10 wt. % of oxygen as starting materials to fabricate ErN spheres. The impurity level was too high. If higher purity ErN is used, the cooling power can be enhanced. In previous works, the volume ratio of Pb/ErN was fixed at 6/4. So, optimization of loading ratio of ErN as regenerator of 4K-GM cryocooler is needed for higher efficient work. Aim of this work is to find the most suitable arrangement of ErN with low oxygen content as regenerator materials for 4K-GM cryocoolers.

2. Experiment
Commercially available Er metallic spheres with 0.07 wt% of oxygen (Santoku Corporation) were classified by sieves. ErN spheres were synthesized by nitriding the Er metallic spheres with different sizes in the hot isostatic pressing method in nitrogen atmosphere (1550°C and 195 MPa of 99.9999% nitrogen). Formation of ErN was confirmed by the X-ray diffraction. The specific heat of ErN was measured by PPMS (Quantum Design). Cooling tests were performed using a commercially available two-stage GM cryocooler (Model SRDK-101D, Sumitomo Heavy Industries Ltd.) with nominal cooling power of 0.1 W at 4.2 K. The operating conditions were the standard ones provided by supplier. The second regenerator column consists of packed Pb spheres, 212-300 μm diameter, together with the cryogenic magnetic regenerator. The initial regenerator material of HoCu2 (180-300 μm in diameter) was replaced by ErN spheres with different sizes. The weights of the ErN regenerator materials loaded in the column were measured. Oxygen content of Er metal, size range and loading ratio of the regenerator materials loaded in the second regenerator column are summarized in Table 1.

By varying the input power to a heater attached to the cold head and monitoring the equilibrium temperature, \( T \), cooling power (CP) versus \( T \) curves were obtained. The lowest achieving temperature was determined when \( CP = 0 \).

Table 1  Summary of regenerator materials in the second regenerator column of 4K-GM cryocooler

| No. | Regenerator | Oxygen content of Er as starting material (wt%) | Size (μm) | Volume loading ratio Pb : HoCu2 : ErN |
|-----|-------------|-----------------------------------------------|-----------|--------------------------------------|
| 1*  | ErN         | 1.10                                          | 180-212   | 6 : 0 : 4                             |
| 2   |             | 0.07                                          | 150-180   | 8 : 0 : 2                             |
| 3   | HoCu2       | --                                            | 180-300   | 6 : 4 : 0                             |
| 4*  | ErN         | 0.07                                          | 150-180   | 7 : 0 : 3                             |
| 5   | ErN         | --                                            | 180-300   | 5 : 0 : 5                             |
| 6   | HoCu2       | --                                            | 180-300   | 5 : 5 : 0                             |
| 7   | HoCu2, ErN  | 0.07                                          | 180-300   | 7 : 2 : 3                             |
| 8   |             | --                                            | 150-180   | 5 : 4 : 1                             |
| 9   |             | --                                            | 150-180   | 5 : 4 : 1                             |
| 10  |             | 0.07                                          | 180-300, 150-180 | 5 : 4 : 1 |
| 11  |             | 0.07                                          | 180-300   | 5 : 4 : 1                             |
| 12  |             | 0.07                                          | 150-180   | 5 : 4 : 1                             |

*Ref. 7  * Commercially available condition

3. Results and discussion
In Fig. 1, the XRD pattern of the obtained nitride sample is shown. This graph indicates that monophase of ErN was obtained. In this figure, XRD pattern of ErN prepared from Er metal spheres with 1.10 wt% of oxygen, which was used in previous work, also appears. In the pattern of the ErN with high oxygen content, the peak assigned by erbium oxide is recognized around 28°.

Temperature dependence of specific heat of ErN with different oxygen content is given in Fig. 2.
Comparing to high oxygen content ErN, low oxygen content ErN shows steeper and larger peak of specific heat around 4 K. ErN specific heat of the low oxygen content indicates the essential specific heat of ErN. When the oxygen content is large, the oxygen atoms solute interstitially in nitride lattice. Thus, the peak of specific heat of ErN was broadened. The oxygen content is important factor to prepare ErN with large heat capacity.

Figure 3 indicates temperature dependence of CP of the GM cryocooler, in which ErN were loaded when volume ratio of Pb to ErN was 6 to 4. Higher CP was obtained at 4.2 K when ErN with lower oxygen content with the same sphere size was used. Comparing to the difference of size, higher CP was obtained using smaller size of ErN. However, higher CP was obtained when HoCu₂ which were loaded in commercially available GM-cryocoolers was used.

To find the optimum volumetric loading ratio of ErN (0.07 wt. %, 150-180 μm) in second regenerator column, the ratio $x$ (Pb : ErN = 10 - $x$ : $x$) was changed 2 to 5. Figure 4 shows CP at 4.2 K as a function of loading ratio $x$ of ErN. The CP at 4.2 K increased with increasing the loading ratio of ErN. However, the results were inferior compared with a case using HoCu₂. Figure 5 shows the loading ratio $x$ dependence of the achieving lowest temperature. The lowest temperature is falling down with increasing loading ratio of ErN. However, the results were also inferior compared with a case using HoCu₂.
We explain the reason why inferior CP was obtained at 4.2 K using ErN in spite of higher specific heat of ErN at 4.2 K comparing to that of HoCu$_2$. In Fig. 2, heat capacities of HoCu$_2$, He gas (1 MPa), and Pb as a function of temperature are also given. He gas shows large heat capacity in the temperature range from 5 to 11 K and a peak around 8 K. HoCu$_2$ can reserve heat in this temperature though ErN and Pb cannot reserved enough. Thus, combination of only ErN and Pb does not realize higher CP than that of HoCu$_2$ and Pb.

To compensate small specific heat of ErN and Pb around the peak temperature of the specific heat of the He gas, HoCu$_2$ was inserted between ErN and Pb. Because both ErN and HoCu$_2$ show the highest CP at $x = 0.5$ (Pb: ErN or HoCu$_2$ = $10 - x : x$) as shown in Fig. 4, the loading ratio of Pb was

![Cooling power of 4K-GM cryocooler using combination of Pb and ErN or HoCu$_2$ with different loading ratio $x$.](image1)

![Achieving lowest temperature of 4K-GM cryocooler using combination of Pb and ErN or HoCu$_2$ with different loading ratio $x$.](image2)

![Cooling power of 4K-GM cryocooler using combination of Pb, HoCu$_2$ and ErN with different loading ratio $x$.](image3)

![Achieving lowest temperature of 4K-GM cryocooler using combination of Pb, HoCu$_2$ and ErN with different loading ratio $x$.](image4)
fixed at 5 and those of ErN and HoCu$_2$ were changed. Figure 6 shows the CP at 4.2 K as a function of loading ratio $x$ (Pb : HoCu$_2$ : ErN = 5 : 5 $- x$ : $x$). The peak value can be found at $x = 1$ where the CP reaches 0.318 W. The loading ratio dependence of achieving lowest temperature is given in Fig. 7. The achieving lowest temperature is almost constant until loading ratio $x$ becomes 3. When $x$ exceeds 3, the lowest temperature rises.

The fact that only replacement of 20% of HoCu$_2$ by ErN leads to increasing rate on the CP of 36% against commercially available regenerator alignment allows the energy-saving and downsizing of 4K-GM cryocoolers.

4. Summary

To enhance cooling power at 4.2 K of GM cryocoolers, ErN spheres were prepared for regenerator materials.

- Large specific heat with a steep peak was observed for ErN spheres with low oxygen content.
- Higher cooling power was obtained using ErN spheres with lower oxygen content.
- When 20% of HoCu$_2$ were replaced by ErN at cold end in the second regenerator column, the cooling power at 4.2 K reaches 0.318 W. This value was 1.36 times as high as that of the GM cryocooler with commercially available regenerator arrangement (using HoCu$_2$).

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