Correlation between cooling power and heat quantity of Er-Ho binary nitride as regenerator of 4K-GM cryocooler

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Abstract. Advanced regenerator materials of erbium and holmium binary nitrides, Er,H0x,N (x = 0 - 1) were studied. Its specific heat vs. temperature curve, possesses a peak due to the magnetic phase transition at their Curie temperature. The cooling power at 4.2 K of a commercial 4K-GM cryocooler filled with the binary nitride of x = 0.625, 0.75, 0.875 or 1 was evaluated. It was found that the cooling power at 4.2 K has a good linear correlation with the heat quantity, which is calculated by integrating C with respect to T in the region of 4.2 – 7.0 K. Three binary nitrides (x = 0.625, 0.875 and 1) filled in series along the regenerator column gave 26% higher cooling power than that filled with HoCu2.

1. Introduction
Cryogenic coolers equipped with a regenerator such as pulse tube coolers and Gifford-McMahon (GM) coolers have been widely used for many systems, high-vacuum pumps and helium liquefaction for systems using superconducting magnets. Current 4K-GM coolers consume an electrical input power as much as several kW to obtain 1 W of cooling power (CP) at 4.2 K. It is required to enhance the energy efficiency from the viewpoints of the energy saving, size reduction and quick cooling. The GM cryocooler has usually two cylindrical regenerators arranged in series, and helium gas goes through the regenerators undergoing compression and expansion to generate the chill. The first regenerator located on the warmer side is filled with copper meshes, and the second one with two materials Pb and HoCu2 spheres on the warmer and colder sides, respectively. HoCu2 is now employed in almost all the commercial 4K-GM coolers as the cold end material because of its large specific heat around the cryogenic temperatures. The CP around 4 K thus depends on the specific heat of the material located on the cold end in the regenerator. Therefore, an advanced regenerator material was developed by referring specific heat values around 4 K [1-4].

We have reported rare earth nitrides (ErN, HoN, DyN, TbN and GdN) are ferromagnetics exhibiting large magnetic specific heats peaking in the low temperature region [5, 6], and proposed as a candidate material for the advanced regenerator. Among them, ErN has a specific heat vs. temperature (C-T) curve peaking at 4 K, which well exceeds that of HoCu2 up to 5 K. Spherical ErN sample was prepared and substituted for HoCu2 in a commercial 4K-GM cryocooler [7]. But this sample was only crude one involving pores and burrs on the surface. The roughness acted as steric hindrance and reduced filling density of the material in the regenerator column, so that CP was degraded. The roughness was reduced by using high purity resource material and removing it by ultrasonic agitation. Furthermore, we employed binary nitrides Er,H0x,N (x=0, 0.5, 0.75, 1.0), and succeeded in obtaining a CP at 4.2 K
(CP@4.2K) larger than of HoCu$_2$ with Er$_{0.75}$Ho$_{0.25}$N [8, 9]. The addition of Ho made the peak shift toward a higher temperature to locate at 6 K and broader than of ErN. In addition, we have demonstrated CP@4.2K larger than of HoCu$_2$ by placing ErN spheres at the cold end of the second regenerator column followed by HoCu$_2$ and Pb in series [10]. These results well indicate that specific heat of regenerator material should be higher not only around 4 K but also over a temperatures region somewhat higher than it. This law is obvious but qualitative, so that some quantitative description is required for searching for the better regenerator. In this work, we prepared two binary nitrides ($x = 0.625, 0.875$) and executed cooling tests. The purpose is to clarify the dependency of CP@4.2K on $x$ in Er$_x$Ho$_{1-x}$N and to investigate its correlation with the features of their $C$-$T$ curves.

2. Experiments

In this work nitride sphere samples were synthesized by nitriding binary alloy spheres of Er$_x$Ho$_{1-x}$ ($x = 0.625$ or $0.875$) using a hot isostatic pressing (HIP) device, O$_2$-Dr.HIP, in which the spheres were held in 180-MPa N$_2$ at 1550 °C for 1 hour. Detail of this process has been reported in previous paper [7]. The alloy spheres were purchased from the same supplier of the other compositions' spheres of $x$=0, 0.5, 0.625, 0.75, 0.875, 1.0 [7-9]. These spheres were smaller than 180 µm in diameter. The material phase occurring in each sample was examined by grinding it into powder and submitting to an X-ray diffractometer, RIGAKU MiniFlex 600+D/tex Ultra. The surfaces and sizes of these spheres were observed using a SEM, JEOL JSM-7000F. Specific heat $C$ of each sample was measured with a PPMS (Quantum Design Model 6000) at temperatures above 2 K. Cooling tests were performed using a commercial two-stage GM cryocooler (Model SRDK-101D, Sumitomo Heavy Industries Ltd.) with a nominal CP of 0.1 W at 4.2 K. The operating conditions are the standard ones provided by the supplier. Its second regenerator column was originally filled with spheres of Pb and HoCu$_2$ with diameter of 0.212-0.3 mm and 0.15–0.30 mm on warmer and colder sides, respectively. The length filled with the HoCu$_2$ was 40% and the remainder was with Pb. The HoCu$_2$ was replaced with the nitride sample with each $x$, and resultant CP was measured. For comparison, CP was also measured when three nitrides, $x$=0.625, 0.875 and 1, were arranged in series along length of 17%, 15% and 8% of the column, respectively. CP was determined as the power inputted to a heater attached to the cooler’s cold head when monitored temperature showed a plateau at $T$ after varying the power. Amount of actually loaded nitride was weighed, indicating that they filled only 52-54% of the space for the regenerator materials, while HoCu$_2$ filled 62%. These less occupations by the nitrides are ascribed to their less smooth surfaces.

3. Results and discussion

The SEM observation showed that the present two samples have almost same size and roughness with the previous ones. Their X-ray diffraction patterns of the both indicated occurrence of mono-nitride with the NaCl type structure and included no peak due to impurity such as oxide, as found in previous work [8,10]. The diffraction peaks clearly showed shifts toward higher angle direction with adding Ho, which is a clear evidence of occurrence of binary solid solutions of ErN and HoN. In figure 1 specific heat data sets are shown as C-$T$ curves together with those measured in the previous work and with that of HoCu$_2$ for comparison. It shows that the peak of the nitride sample shifts toward higher temperature direction with increasing Ho-content, and the peaks of the binary nitrides are significantly broader and lower than those of HoN and ErN. In figure 2 their peak-top temperatures found in these C-$T$ curves are plotted against $x$. An excellent linear relation is obtained. Thus we have successfully obtain a series of nitride regenerator materials with continuously varying magnetic transition temperature in a range between 4 and 13 K. figure 3 shows CP vs. $T$ curves measured for binary nitride Er$_x$Ho$_{1-x}$N and HoCu$_2$ in temperature regions of (a) 2 - 15 K and (b) 2 - 7K. CP@4.2K measured with HoCu$_2$, 0.23 W at 4.2K, exceeds the nominal cooling power of this cryocooler, since we have replaced the initially installed materials with other ones.
Figure 1. Specific heat vs. temperature curves of Er$_x$Ho$_{1-x}$N, HoCu$_2$ and Pb.

Figure 2. Peak-top temperature in $C$-$T$ curves of Er$_x$Ho$_{1-x}$N with various $x$.

In figure 4 $CP$ at 4.2 K are plotted against composition $x$ in Er$_x$Ho$_{1-x}$N. $CP@4.2K$ of $x = 0.625$, 0.875 did not exceed that with $x = 0.75$.

To find a key factor for enhancing $CP@4.2K$ from their $C$-$T$ curves, we focused on the heat quantity of the samples from 4.2 K to a somewhat higher than it, $T_H$. It is denoted as $HQ(4.2, T_H)$ and was calculated by integrating the $C$-$T$ curve in figure 1 with respect to $T$ and by multiplying the amount of the sample loaded into the regenerator column, $V$. In the numerical integrations, the trapezoidal method was employed with temperature step of 0.5 K.

\[ HQ(4.2, T_H) = V \int_{4.2}^{T_H} CdT \]  

(1)
**Figure 3.** Cooling power of 4K-GM cryocooler (Model SRDK-101D by SHI) using Er\(_{x}\)Ho\(_{1-x}\)N and HoCu\(_2\) in temperature regions of (a) 2 - 14 K and (b) 2 - 7 K.

**Figure 4.** Cooling power at 4.2 K obtained with Er\(_{x}\)Ho\(_{1-x}\)N.

CP@4.2K values of these samples were plotted against HQ(4.2, \(T_H\)), and their correlations were investigated by varying \(T_H\) from 5 to 9 K by step of 0.5 K. As a result it was found that the plots against HQ(4.2, 7.0) showed a linear relation as shown in figure 5. The line drawn there was obtained by the least-square method. Note that this linear relation is based on the plots of the six nitrides and HoCu\(_2\), but not of the three nitrides. The coefficient of determination was \(R^2 = 0.985\), and the other \(T_H\) gave significantly lower \(R^2\) values; 0.605(6.0 K), 0.843(6.5 K), 0.935(7.5 K) and 0.812(8.0 K), 0.470(9.0 K). The serial three nitride gave a considerably higher CP than given by the monolithic nitrides, suggesting effectiveness of the arrangement with an appropriate order and relative amounts. In the present trial, the order of the three was set as the peaking temperature on the C-T curve.
Figure 5. Cooling power at 4.2 K plotted against net heat quantity of the materials in temperature region of 4.2 – 7.0 K.

increases with distance from the cold end. Relative amounts of the three were decided as following the highest C among the three, in other word as maximizing HQ(4.2, 7.0) assuming the linear temperature distribution along the column. The resultant CP@4.2K was so enhanced as to exceed the others. It was 12% higher than with x = 0.75, and 26% higher than with HoCu2. However, its plot in figure 5 is located a little below the regression line.

Thus found linear correlation is just an empirical one, but it is simple and would be a useful guideline for searching a new regenerator material and/or arrangement. Its physical background is still vague, and what we can say at present stage is as follows. HQ(4.2, Ti) is the heat reserved by the material in the temperature region, then could be regarded as the maximum heat that we may exploit. Ti may be a kind of representative temperature around which the material works as the regenerator. The validity of this correlation should be checked with different test conditions, for instance, such as of relative filling lengths of regenerator materials. Of course, these results should be examined by comparing with simulations on the temperature distribution and the cooling power [11].

4. Conclusion
We successfully synthesized regenerator spherical materials of binary nitrides, Er,Ho1-x,N (x =0, 0.5, 0.625, 0.75, 0.875 or 1), and executed cooling tests with a commercial 4K-GM cryocooler filled with the nitrides. Obtained cooling power at 4.2K was found to show a linear correlation with the heat quantity of the material from 4.2 to 7.0K. The nitride of x=0.75 gave the highest cooling power at 4.2K, which was higher than HoCu2 gave. A much higher cooling power was given by three nitrides arranged in series, which was 26% higher than by HoCu2 and fairly in accordance with the correlation.

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