A research on silver powder sinters for dilution refrigerator heat exchangers

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Abstract. Due to the Kapitza resistivity, a sharp deterioration of heat transfer occurs between solid and liquid in the heat exchanger of the dilution refrigerator at extremely low temperature. It is necessary to use silver powder sintered heat exchangers to optimize the interface heat transfer. A theoretical calculation of heat exchangers at extremely low temperature was carried out to analyze the influence of the Kapitza resistivity on heat transfer performance. Silver powder with different particle sizes of 80 nm, 200 nm and 500 nm were selected for the preparation of sinters. Their micro-scale sintering conditions, pore volumes and specific surface area were carefully presented. It can be concluded from the theoretical calculations and the experimental results that the 200 nm silver powder sinters can optimize the performance of dilution refrigerator heat exchanger with a large heat exchange area.

1. Introduction
Since the twentieth century, cryogenic scientists have been constantly exploring cryogenic materials and equipment. With the advantages of low magnetic field and light weight, dilution refrigerators have become the general method to obtain a temperature lower than 100 mK in terms of quantum computer field. As one of the core components, the sintered heat exchanger is critical for the performance of dilution refrigerators especially at temperature below 10 mK [1-2], for 3He fluid must be pre-cooled well to obtain an ultralow temperature in the mixing chamber.

There are many factors which should be taken into consideration on the design of heat exchangers at extremely low temperature. At first, the working fluid tends to behave abnormally at low temperature, so it is essential to investigate low-temperature physical properties, such as viscosity, thermal conductivity, and Kapitza resistivity [3-4]. The second is the basic structure design of silver powder sinters to meet the heat-exchanger requirements according to the parameters of the working fluid and the working conditions of the dilution refrigerator. Thus, the heat transfer performance can be verified and optimized through theoretical and experimental analysis. Taking the above conditions...
into account, studies on calculations of the thermal performance of dilution refrigerator heat exchangers and preparation optimization on silver powder sinters were carried out as discussed below.

2. Heat exchanger model

2.1. Structural model

In a dilution refrigerator, the heat-exchanger models are usually sintered types or sleeve types between the still and the mixing chamber, according to different heat-exchange area requirements. The structural model was improved on the sintered copper powder heat exchanger with the tubular structure by Ran [5], as shown in Figure 1. In our preliminary design, silver powder was used to replace copper powder as sinter material. The diameters of the working fluid channel in sinters were 1 mm for the concentrated phase and 2 mm for the diluted phase.

![Figure 1. The structure of the heat exchanger [5]](image)

Heat exchange in the axial direction relies on the thermal conductivity of the working fluid and the CuNi tube at extremely low temperature. The central liquid channel greatly reduces the flow resistance, thus reducing the viscous heat. The structural parameters were further discussed by theoretical calculations in the next part.

2.2. Thermal calculation

Considering the actual situation of the dilution refrigerator, some assumptions on the model of the counterflow heat exchanger were made, as listed below,

1. The temperature of the still $T_s$ is 700 mK.
2. The cooling capacity $Q$ and the flow rate are constant.
3. Due to the existence of the central flow channel, it is reasonable to ignore the influence of the sintered body on the flow resistance.
4. Inside the pipeline, the flow of working fluid is steady, and the temperature distribution is uniform.

According to the conservation of energy, the thermal calculation expression of the counterflow heat exchangers from the still to the mixing chamber is obtained by equations in literature [6]

Diluted phase:

$$A_p \frac{d}{dx} \left( \lambda_d \frac{dT_D}{dx} \right) + \eta_d (\dot{n}v_D) \frac{dZ_D}{dx} + \frac{P(T_c^4 - T_D^4)}{4R_{KM}} = \dot{n}C_D \frac{dT_D}{dx}$$

Concentrated phase:

$$A_c \frac{d}{dx} \left( \lambda_c \frac{dT_c}{dx} \right) + \eta_c (\dot{n}v_c) \frac{dZ_c}{dx} + \frac{P(T_c^4 - T_D^4)}{4R_{KM}} = \dot{n}C_c \frac{dT_c}{dx}$$

Where the three terms on the left side of the Equation 1 and Equation 2 represent the axial heat conduction, viscous heating and lateral interface heat transfer, respectively. The lateral interface heat transfers through the two sections of Kapitza resistivity between the pipe wall and the liquid on both sides of wall, and the average Kapitza resistivity $R_{KM}$ is obtained from the sum of the above two.
Where \( A \) is the cross-sectional area of the fluid pipeline, \( \lambda \) is the thermal conductivity of fluid, \( Z \) is the flow resistance in pipeline, \( \eta \) is the viscosity coefficient of fluid, \( v \) is the fluid specific volume, \( P \) is the effective perimeter of the heat exchanger and \( C \) is the specific heat capacity of fluid. In the formula, subscript \( C \) represents the parameters on the concentration side and subscript \( D \) represents the parameters on the dilution side.

Under extremely low temperature conditions, the effects of viscosity and heat conduction of the working fluid in the counterflow pipeline are completely different from that at room temperature. The properties of the concentrated and diluted phase are listed in Table 1.

**Table 1. The properties of the concentrated and diluted phase [7]**

| Properties                        | The concentrated phase | The diluted phase |
|-----------------------------------|------------------------|------------------|
| Enthalpy/J·mol\(^{-1}\)K\(^{-2}\) | 12.5\(T^2\)           | 94.5\(T^2\)     |
| Molar volume of \(^3\)He/cm\(^3\) | 36.86                  | 424.4            |
| Viscosity coefficient/\(\mu\)P | 2.2\(T^2\)+26.3\(T^{-1/3}\) | 0.5\(T^2\)     |
| Thermal conductivity/\(\mu\)J·cm\(^{-1}\)s\(^{-1}\)deg\(^{-1}\) | 3.3\(T^1\)            | 2.4\(T^{1/2}\) |

Discretizing the heat transfer formula by the micro-element method, 0.0001K is taken as one step. The differential operation in the thermal calculation of heat exchanger is sorted into discrete operation \( \Delta t = T_K - T_{K-1} \).

\[
T_K = 0.700 - Kt, K=0,1,2,3...6900 \tag{3}
\]

Taking heat transfer calculation of the concentrated phase as an example, the integrated discrete formula can be given by

\[
\frac{A}{\Delta x_K} + (B + C)\Delta x_K - D = 0 \tag{4}
\]

\[
A = \lambda_{ck} A_c (T_K - T_{K-1}) \tag{5}
\]

\[
B = \eta_{ck} (\dot{\eta} v_c)^2 \frac{128}{\pi d_c^2} \tag{6}
\]

\[
C = S_c \left( 1 - \frac{a^2}{b^2} \right) \frac{T_k^4}{4 R_{km}-x} \tag{7}
\]

\[
D = i a T_k (T_K - T_{K-1}) \tag{8}
\]

Where \( d_c \) is the diameter of the concentrated phase flow channel, \( S_c \) is the interface heat transfer area per unit distance, and \( a \) and \( b \) are the correlation coefficients of the two-phase enthalpy. Using the MATLAB calculation platform, the heat transfer distance required for each temperature step can be obtained and the total length of the heat exchanger can be summed by

\[
X_i = \sum_{k=0}^{i} \Delta x_k \tag{9}
\]

This discrete formula allows to simulate the heat transfer process of an extremely-low-temperature counterflow heat exchanger in complex axisymmetric geometries. However, due to the inaccuracy of helium properties at very low temperature, there may be large deviation in the calculation results below 10mK.

### 2.3 Simulation results

Through the above calculation methods, it has been carried out that simulation calculations for the three types of heat exchangers. As shown in Figure 2, the solid square curve represents the performance of all sintered heat exchangers in the whole section, the hollow square represents all sleeve type and the hollow circle presents a mix of the above two. It is worth mentioning that the solid circle curve represents heat transfer of the sleeve style, ignoring heat conduction and viscous heat. According to the simulation results, it can be seen that the sintered heat exchanger exhibits a low dependence on the heat exchange area around 200 mK. In Figure 3, when the temperature is lower
than 137 mK, the demand for the heat exchange area of the sleeve exchanger increases rapidly. If the minimum temperature of dilution refrigeration reaches 10 mK, the heat transfer distance required for the all sintered type is only 1.099 m, the hybrid type is 3.7499 m and the sleeve type is much longer. The above results prove that it is difficult for the sleeve heat exchanger to meet the heat exchange area requirements at very low temperature. Even if the silver powder sintered is used, its specific surface area needs to reach at least 1 m²/g.

3. Preparation of materials

3.1. Silver powder sinter
To verify the feasibility of the silver powder sintering model, the first issue is to ensure the excellent performance of the sintered body. Silver powders with different particle sizes were selected as the
materials for sintering. The three sizes were 80 nm, 200 nm and 500 nm, respectively, as shown in Table 2. The mould is composed of stainless-steel cover and bottom, and bolts provide sintering pressure. The powders were sintered at 250°C for one hour under vacuum conditions [8].

| Nominal particle size (nm) | Sample number | Sintering pressure (MPa) | Heating rate (K/min) | Insulation conditions |
|---------------------------|---------------|--------------------------|----------------------|----------------------|
| 80                        | A1            | 15                       | 10                   | 250°C×1h             |
|                            | A2            | 20                       |                      |                      |
|                            | A3            | 40                       |                      |                      |
| 200                       | B1            | 15                       | 10                   | 250°C×1h             |
|                            | B2            | 20                       | 10                   | 250°C×1h             |
|                            | B3            | 40                       |                      |                      |
| 500                       | C1            | 15                       | 10                   | 250°C×1h             |
|                            | C2            | 20                       |                      |                      |
|                            | C3            | 40                       |                      |                      |

3.2. Surface structures
Using SEM-S4800 techniques, images of the silver powders surface morphologies were obtained. Silver powder samples was fixed with conductive tape before observation. The SEM images of A1, B1, C1 at a magnification of 10 k and 50 k were shown in Figure 4. The 200 nm sample has good agglomeration, and the adhesion between particles is uniform, which is in the form of flocs, conducive to the increase of specific surface. There are still obvious particles on the sintered surface of the 80 nm and 500 nm silver powder samples.

To investigate the surface structure, scanning electron microscope (SEM) was performed on of as-prepared silver powder. The SEM images of silver powder with different particle sizes of 80 nm (A1), 200 nm (B1), 500 nm (C1) were shown in Figure 4. The 200 nm sample exhibits good agglomeration with uniform adhesion between particles. The flocs have advantage of increasing specific surface. Obvious larger particles on the sintered surface are observed on the silver powder samples with size of 80 nm and 500 nm.

![Figure 4. Representative SEM images of A1, B1, C1 samples. Scale bars, 5 \( \mu \)m (up) and 1 \( \mu \)m (down)
The SEM images of samples under different sintering pressures were exhibited in Figure 5. At sintering pressure lower than 15 MPa, mechanical strength was insufficient, so it can be separated by hand. On the other hand, in high-pressure region, aggregation would be too strong, resulting in insufficient porosity. Moreover, the specific value of suitable pressure needs further investigations.

3.3. Specific surface areas and total pore volumes
The gas adsorption method is mainly developed by the capillary aggregation phenomenon and the principle of volume equivalent substitution. Under the assumption that the shape of the pore is cylindrical and tubular, the capillary aggregation model is established to estimate the pore size distribution characteristics and pore volume of the samples. The nitrogen adsorption measurement of the sinter samples was performed by Quadrasorb SI-MP apparatus. Taking the limitation of silver sintering temperature into account, the samples were heated at 150 °C to remove water and gas.

According to the results of the test data, the specific surface area and total pore volume of the sinters are determined by the Brunner–Emmet–Teller (BET) measurements and the Barret-Joyner-Halenda (BJH) method, respectively, which were shown in Table 3. For 80 nm and 500 nm samples, the specific surface areas were much less than 1.00 m²/g. However, for 200 nm samples, the specific surface area was up to 1.52 m²/g and total pore volume reached 3.92×10⁻³ cm³/g, which fully met the theoretical calculation assumption of the heat exchanger at extremely low temperature.

Table 3. The specific surface areas and total pore volumes of powders samples

| Nominal particle size (nm) | Sample number | Total pore volumes(cm³/g) | Specific surface areas(m²/g) |
|---------------------------|---------------|---------------------------|-----------------------------|
| 80                        | A1            | 8.20×10⁻⁴             | 0.36                        |
|                           | A2            | 8.83×10⁻⁴             | 0.31                        |
|                           | A3            | 1.03×10⁻³             | 0.24                        |
| 200                       | B1            | 3.92×10⁻³             | 1.52                        |
|                           | B2            | 2.54×10⁻³             | 1.24                        |
|                           | B3            | 3.06×10⁻³             | 0.72                        |
| 500                       | C1            | 6.96×10⁻⁴             | 0.56                        |
|                           | C2            | 1.23×10⁻³             | 0.44                        |
|                           | C3            | 1.05×10⁻³             | 0.32                        |

4. Conclusions
According to discrete calculation method, the design parameters of the counterflow heat exchanger used for dilution refrigerators were analysed, which could guide the design of heat exchangers of dilution refrigerator.

Silver powder sinters with particle sizes of 80 nm, 200 nm and 500 nm were tested to compare the parameters of pore volumes and specific surface area. The specific surface area of the 200 nm reached the 1.52 m²/g, completely better than the other two as sinter material.

The researches on the sintering process need improvement. The peculiar relationship between specific surface area and particle size of silver powder sinters can be further explored. More sintering conditions, such as temperature and pressure, will be tested to find the best material in future.

5. References
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