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A Superconducting Filter to Separate an Oxygen and Argon Mixture

YUICHI SAWAI*
NORIKO BAMBA
KOZO ISHIZAKI
SHIGEKI HAYASHI**
ishizaki@voscc.nagaokaut.ac.jp
Nagaoka Gijutsu-Kagaku Daigaku (Nagaoka University of Technology), Nagaoka, Niigata 940-21, Japan

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Abstract. Hot isostatic pressing in an oxygen atmosphere, known as O_2-HIP method, has been used successfully to synthesize oxide materials, as well as to produce porous materials. In this paper a porous superconducting oxide is synthesized by this method and its application as a gas filter is described. Porous superconductors can be used to separate a mixture of paramagnetic and diamagnetic gases, such as oxygen and argon. Separation occurs after a magnetic field is applied and is based on the Meissner effect. Experimental results showed that the oxygen content of an oxygen/argon mixture increased after passing through a filter with large pore size (about 10 μm).

Keywords: superconducting filter, gas separation, magnetic gradient, Meissner effect

1 Introduction

Since the boiling points of oxygen and argon are similar, it is difficult to remove argon impurities from oxygen using conventional methods. Chemical methods also cannot be used because argon is an inert gas. Oxygen and argon, however, do exhibit different magnetic behavior, paramangnetism and diamagnetism, respectively. This difference can be utilized in separating the two materials.

A magnetic force, F, acting on a material in a magnetic field is given by

$$F = M\frac{dH}{dx} = \frac{M}{\mu_0}\frac{dB}{dx} \tag{1}$$

where H is the magnetic field, B is the magnetic flux density, μ_0 is the relative permeability, and M is the magnetization. Magnetization M is given by

$$M = \chi_m H = \frac{\chi_m}{\mu_0} B \tag{2}$$

where χ_m is the magnetic susceptibility. The magnetic susceptibility of paramagnetic materials (such as oxygen or carbon dioxide) is positive and that of diamagnetic materials (such as argon, nitrogen or water) is negative. Equations (1) and (2) can be rearranged to give

$$F = \frac{\chi_m}{\mu_0^2} B\frac{dB}{dx} \tag{3}$$

According to Eq. (3), if a magnetic field is applied to an oxygen/argon mixture, the force acting on the oxygen molecules is opposite to the force acting on the argon atoms. In other words, a mixture of oxygen and argon can be separated in a magnetic field. It is, however, difficult to obtain a high magnetic gradient (BdB/dx) using a standard permanent magnet or a coil, and therefore a porous superconducting material can be used to overcome this problem.

If an external magnetic field is applied to a porous superconducting filter before cooling down, the magnetic flux passes through the entire material, as shown in Fig. 1(a). The Meissner effect of a superconductor prevents the magnetic flux from passing through the material. If the material is then cooled down below the critical temperature, the magnetic flux only passes through the penetrating pores, as shown in Fig. 1(b). If an external magnetic field is applied after the material is cooled down, the magnetic flux does not pass through the material at all, as shown in Fig. 1(c).

The external magnetic field should be less than the lower critical field, H_{C1}, or else the material will no

*Present Address: The Energy Device Dept., Hitachi Ltd., Hitachi Research Laboratory, 1-1, Saiwai 3, Hitachi, Ibaraki 317, Japan.
**Present Address: Osaka Sanso Kogyo Ltd., 670 Kami, Sakai, Osaka 593, Japan.

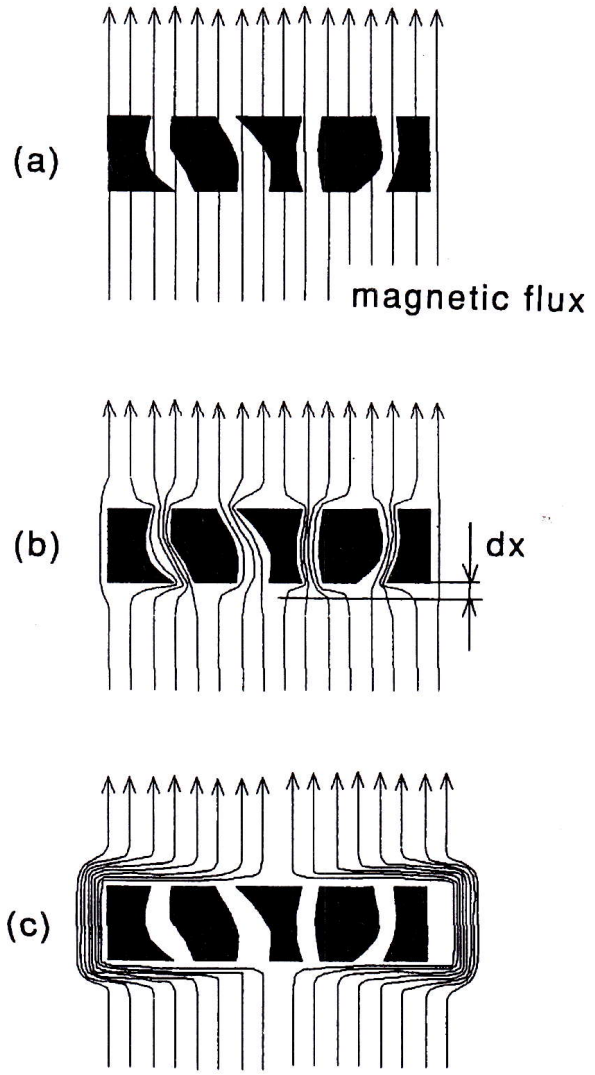

Fig. 1. Magnetic flux around the porous superconducting filter. (a) magnetic flux before cooling down the superconducting filter, (b) magnetic flux after cooled to a temperature lower than the critical temperature from the state (a), and (c) magnetic flux applied after cooling down the filter. Note that magnetic flux is concentrated in pores in (b), and the gradient of magnetic flux becomes higher at the surface of pores of the superconducting filter. Pore diameter should be larger than the London penetration depth, λ.

longer be superconducting. In Fig. 1(b) the magnitude of the magnetic flux density in the vicinity of a hole is higher than that of the outside, and thus the gradient of the magnetic flux density on the surface of the superconducting material becomes very high. The pore diameter must be larger than the penetration depth of London, λ, about 150 nm [1]. If the diameter of the penetrating pores is less than this depth, the magnetic flux passes through the superconducting body adjacent to the pore within the limits of this depth. Thus, the magnetic flux cannot be concentrated in the pores, and cannot generate a large separating force.

To obtain a high magnetic gradient (BdB/dx), the effective length (dx) in Fig. 1(b) should be small enough to create a high value of BdB/dx. A porous superconducting material is capable of generating such a high magnetic gradient. The magnetic flux density passing through the penetrating pore, B_{pore}, is always higher than that of the external flux density, B_{out}. Then B_{pore} is given by

$$B_{\text{pore}} = K B_{\text{out}} \qquad (K > 1) \tag{4}$$

The value of K is a function of the geometric shape of the pores, and is approximately 4–10 when the open porosity is about 0.3 (see Appendix). This means B_{pore} is at least 4 times higher than B_{out}. A superconducting material with a high T_c and reasonably high H_{C1} is required. The 123 phase ($YBa_2Cu_3O_{7-x}$) has these properties and is useful for this experiment.

Reich et al. have already shown that a superconducting membrane can be used to separate gases that have a substantial difference in paramagnetism. A porous 123 membrane was used with an average pore diameter of less than 1 nm. They demonstrated that oxygen (a paramagnetic substance) could be separated from nitrogen (a diamagnetic material) using the mirror principle. Better filtration results were achieved without a magnetic field than with it. When an external magnetic field was applied, the separating force was reduced [2, 3]. Clearly they did not make use of the Meissner effect. We believe that the pore diameter of their sample is too small to develop a large separating force even when the magnetic field is applied after cooling down. Moreover the porous materials with nanopores are not easy to produce. The pore size should be larger than the penetration depth (about 150 nm) if the Meissner effect is to be used.

In this paper, it will be shown that applying an external magnetic field to a porous superconducting material with large sized pores enhances the separation mechanism. By applying an external magnetic field, the magnetic force acting on the oxygen and argon molecules is generated whenever large-sized pores are used. It was confirmed that a porous superconducting material with few μm sized pores are useful for gas separation, but the optimum pore diameter was not obtained. Note that this force does not depend on the mirror principle.

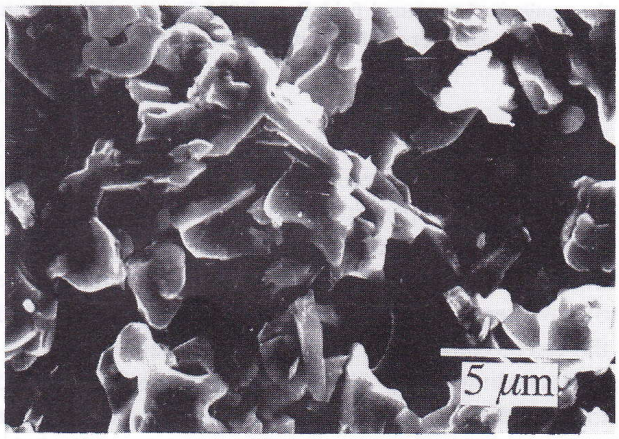

Fig. 2. Scanning electron micrographs of the surface of a porous superconducting filter.

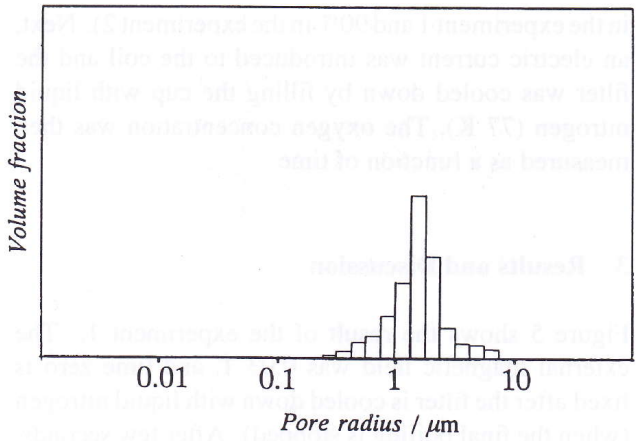

Fig. 3. Pore size distribution of a porous superconducting filter measured by the mercury porosimetry method.

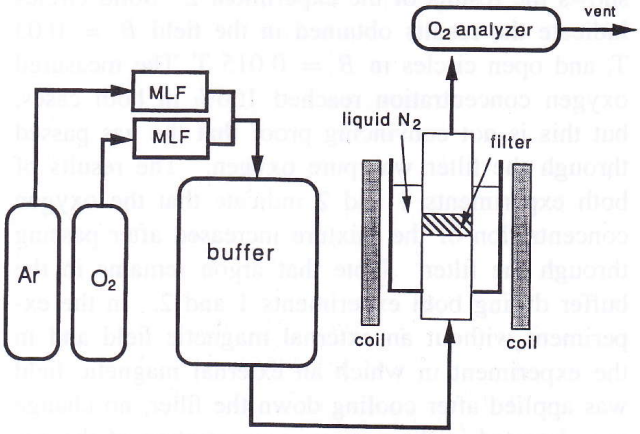

Fig. 4. Schematic illustration of the experimental system. MLF indicates mass flow meter. The buffer reduces the pressure increase in the system caused by argon which cannot pass through the 123 filter.

2 Experimental Procedure

Powder of the 123 phase was ground by a mortar, screened through a 330-mesh (less than 45 μm), shaped into a disk, and O_2-HIP treated to create open pores [4] under high oxygen partial pressure to keep the 123 phase as superconducting phase [5]. O_2-HIPing was carried out at 1000°C, under 200 MPa of the total gas pressure in a 1% oxygen and argon mixture (i.e. the oxygen partial pressure was 2 MPa) for 5 h [5]. The disk was then annealed at 400°C in air for 24 h and used as the filter. Scanning electron micrographs of the surface of the filter and its pore size distribution are shown in Figs. 2 and 3, respectively. Open porosity of the filter was 0.4 and mean pore diameter was 2μm.

Figure 4 shows a schematic representation of the experimental system. An oxygen and argon mixture is introduced to the buffer. The mixing ratio is controlled by the mass flow controller (STEC Co., model SEC-400MK3). The mixture passes through the filter and into the oxygen analyzer (Osaka Sanso Kogyo Ltd., model OM2-B).

The experiments were carried out using two kinds of oxygen/argon mixture. A 50% oxygen and 50% argon mixture was used in the experiment 1, and a 90% oxygen and 10% argon mixture in the experiment 2. The total flow rate of the oxygen and argon mixture was about 0.03 m^3s^{-1}.

After 30 minutes of flow, all the gas in the buffer was completely replaced by the oxygen and argon mixture. The pressure of the mixture in the buffer was 0.125 MPa (950 mmHg). At this moment, the oxygen analyzer indicated the initial oxygen content of the mixture (50%

in the experiment 1 and 90% in the experiment 2). Next, an electric current was introduced to the coil and the filter was cooled down by filling the cup with liquid nitrogen (77 K). The oxygen concentration was then measured as a function of time.

3 Results and Discussion

Figure 5 shows the result of the experiment 1. The external magnetic field was 0.03 T, and time zero is fixed after the filter is cooled down with liquid nitrogen (when the final boiling is stopped). After few seconds, oxygen concentration increased up to 68%, and at 40 s, the concentration decreased to 61%. This concentration then held constant for more than 160 s. Figure 6 shows the results of the experiment 2. Solid circles indicate the results obtained in the field $B = 0.03$ T, and open circles in $B = 0.015$ T. The measured oxygen concentration reached 100% in both cases, but this is not convincing proof that the gas passed through the filter was pure oxygen. The results of both experiments 1 and 2 indicate that the oxygen concentration of the mixture increased after passing through the filter. Note that argon remains in the buffer during both experiments 1 and 2. In the experiment without an external magnetic field and in the experiment in which an external magnetic field was applied after cooling down the filter, no change was detected in the oxygen concentration of the gas mixture.

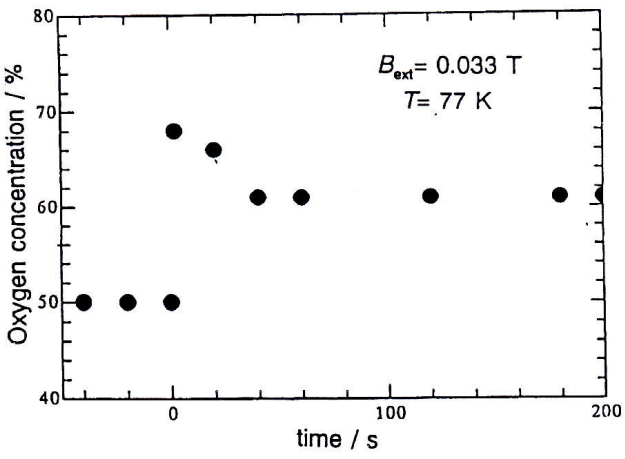

Fig. 5. Oxygen concentration after passing through the 123 filter. 50% oxygen and 50% argon mixture was used. Temperature was fixed at 77 K and the external magnetic filed was 0.03 T. The flow rate of the mixture was about 0.03 m^3s^{-1}. Time zero is the moment when the initial violent boiling stops.

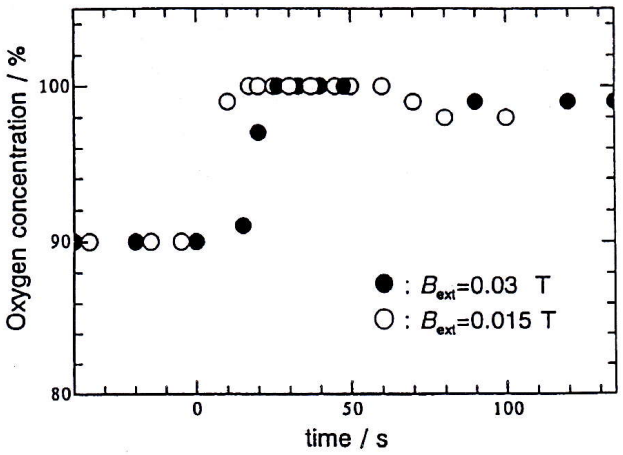

Fig. 6. Oxygen concentration after passing through the 123 filter. 90% oxygen and 10% argon mixture was used. Open circles indicate the results in the external field $B = 0.015$ T and solid circles in $B = 0.03$ T. All other conditions were same as in Fig. 5.

The increase followed by a decrease in oxygen concentration at the beginning of cool down in Fig. 5 may be due to the temperature of the gas mixture. The oxygen/argon gas mixture at room temperature was introduced to the filter continuously causing the temperature of the filter to increase slightly. The oxygen content of the gas passing through the filter then decreased.

According to Eq. (3), oxygen molecules are forced to enter the penetrating pores but remain in the pores because the magnitude of BdB/dx at the end of the pores is equal to but opposite to that of the field at the entrance. The experiment was successful because the pressure at the pore exit was ambient (760 mmHg), whereas the pressure at the entrance was higher (950 mmHg).

The authors believe that the technique described above can be applied for pure argon production. Since the product, in this case, is argon which remains in the buffer (not oxygen which passes through the filter), each impurity oxygen molecule must approach the surface of the filter impartially, and the system shown in Fig. 4 should be arranged. Thin and porous filter with high strength is also necessary.

4 Conclusion

A superconducting filter to separate argon from oxygen has been demonstrated. Separation is achieved by applying a magnetic field to the filter. The Meissner effect prevents the magnetic flux from passing

through the material. If the porous superconducting filter is cooled down after a magnetic field is applied, the magnetic flux is concentrated through the penetrating pores and therefore the gradient of the magnetic flux density, which is proportional to the magnetic force acting on each molecule, becomes very high at the surface of the filter. By applying a magnetic field, pores of large size can be used to separate the mixture.

Appendix: Pore Configuration Factor

Calculation of the pore configuration factor K from the open porosity is as follows. It is assumed that the filter is thin enough so that the cross sectional area of a penetration pore is almost constant through the pore. The shape of a penetrating pore is assumed to be straight. The configuration factor, K is given by

$$K = \frac{A_{\text{tot}}}{\Sigma A_{\text{pore}}} \tag{5}$$

where A_{tot} is a projection area of the filter and A_{pore} is a cross sectional area of a penetrating pore as shown in Fig. 7. The open porosity of the porous material is given by

$$P_o = \frac{V_o}{V} \tag{6}$$

where V_o is the total volume of the open pore and V is the volume of the porous material. The volume of the penetrating pores, V_p, is given by $V_p = \gamma V_o$, where γ has value between 0.3 and 0.8 [6], and K can be calculated as

$$K = \frac{A_{\text{tot}}}{\Sigma A_{\text{pore}}} \simeq \frac{V}{V_p} = \frac{1}{\gamma P_o} \tag{7}$$

Assuming that the open porosity is 0.3, this value is calculated to be between 4–10. Since the real pores are not straight, the true value for porous materials probably exceeds 10.

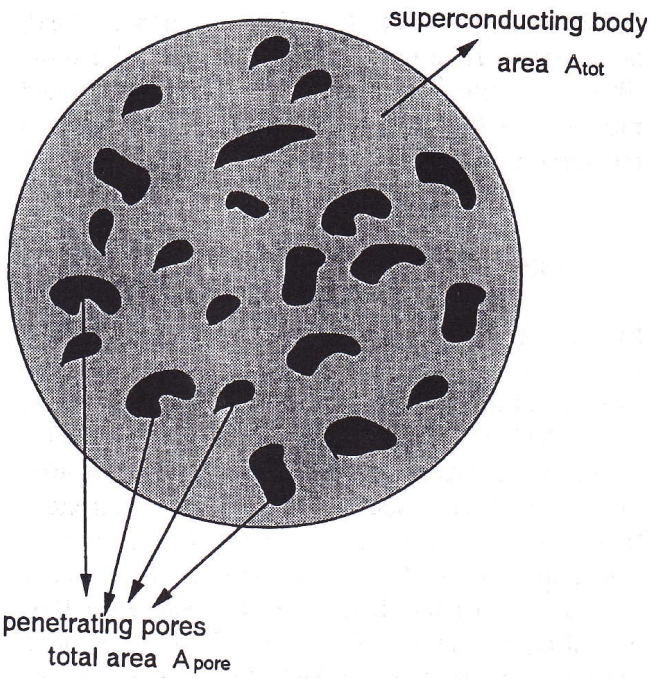

Fig. 7. Schematic illustration of the distribution of penetrating pores in the superconducting body. A_{pore} is the total area of penetrating pores and A_{tot} is the total projection area of the filter. Magnetic flux passes through penetrating pores and not through the superconducting body, thus the magnetic flux density in pores is concentrated by the factor $(A_{\text{tot}}/A_{\text{pore}})$.

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