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Magnetic susceptibility of oxygen adsorbed on the surface of spherical and fibrous activated carbon

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The magnetic susceptibilities of oxygen adsorbed on the surface of bead-shaped activated carbon and activated carbon fibers were evaluated as a function of temperature between 4.2 K and 300 K, and found to exhibit a sharp peak at around 50 K. This implies that the adsorbed oxygen molecules form an antiferromagnetic state. The relation between the susceptibility and the adsorbed mass suggest that the thickness of the adsorbed oxygen is thin enough to consider a two-dimensional structure for bead–shaped activated carbon and carbon fibers across the fiber axis but thick enough to regard it as three-dimensional along the fiber axis. The result is discussed with reference to the study on one-dimensional oxygen array.

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1. Introduction :

In our laboratory, magnetic susceptibility of various carbon and graphite materials has been measured as a function of temperature between 4.2 K and 300 K [1 - 4]. We have observed that the diamagnetism of such a defective and porous carbon material as activated carbon shows a sharp positive peak at around 50 K against temperature and becomes apparently paramagnetic below 100 K under oxygen pressure. This behavior has been considered to be due to the adsorption of oxygen on the surface of defective carbon [5]. However, the mass of adsorbed oxygen was not measured as a function of temperature and the magnetic susceptibility of adsorbed oxygen could not be evaluated.

In the present work, spherical bead-shaped activated carbon and activated carbon fibers are chosen as host materials, because activated carbon is a well- known industrial material widely used in the field of environmental engineering on account of its high adsorption capacity. Moreover, activated carbon is an ideal host material to study magnetic properties of various guest molecules absorbed on its surface, in particular, their temperature dependence, because the magnetic susceptibility of activated carbon is small in magnitude and constant against temperature. Both spherical and fibrous shapes of activated carbon are adopted in order to study the anisotropy of the magnetism of adsorbed oxygen on the surface of carbon fibers along and across the fiber axis.

The magnetic susceptibility was measured as a function of temperature between 4.2 K and 300 K with constant monitoring of mass of adsorbed oxygen under various oxygen pressures that were controlled at room temperature.

The susceptibility showed a positive peak at around 50 K and the susceptibility of the adsorbed oxygen was successfully evaluated as a function of temperature. The results implied that the adsorbed oxygen molecules form an antiferromagnetic state.

The susceptibility of the adsorbed oxygen depends on the adsorbed mass of oxygen for the case of spherical bead-shaped activated carbon, which is also observed for carbon fibers measured in perpendicular to the fiber axis. However, the susceptibility of adsorbed oxygen is independent of the adsorbed mass of oxygen for the fibers measured in parallel to the fiber axis. This anisotropy of the susceptibility-mass relation is considered to be derived from the difference in thickness of the adsorbed oxygen molecules in perpendicular and parallel to the fiber axis. The experimental results are compared with those of oxygen molecules adsorbed on the surface of highly crystalline graphite and also with that of one-dimensional oxygen array formed inside an artificially synthesized molecule [6].

2. Experimentals :
2.1 Specimens and methods :

Spherical activated carbon employed in the present work was bead-shaped activated carbon manufactured by Kureha Chemical Industry, Japan. The bead diameter was 0.4 mm. The specimen was placed in a quartz basket during the susceptibility measurements. Activated carbon fiber examined in this work was manufactured by UNITIKA, Japan, its trade name being AD'ALL. The specimen type was A-7. A bundle of carbon fibers was tied with silk threads and the cross sectional area was fixed with an

adhesive to avoid oxygen adsorption on the cross section of the fibers.

Magnetic susceptibility was measured by the Faraday method using a Cahn R2000 electrobalance. Temperature was controlled with an Oxford ITC503S between 4.2 K and 300 K. Oxygen pressure was controlled at room temperature from 6.4×10^{-2} Pa to 2.7×10^{2} Pa. The mass of the specimen was constantly monitored by the balance during the measurement. For the fibers, the susceptibility measurement was carried out in both perpendicular and parallel to the fiber axis.

2.2 Results and Discussion :

The magnetic susceptibility of activated carbon was about -1.0×10^{-6} emu/g and was temperature independent, which is typical of carbon materials with low crystallinity [5].

Figure (1) shows the magnetic susceptibility of bead-shaped activated carbon as a function of temperature between 4.2 K and 300 K under an oxygen pressure of 1.6×10^{2} Pa controlled at room temperature. The susceptibility exhibited a sharp peak at around 50 K and the specimen became paramagnetic in this temperature region. This is considered to be due to the oxygen adsorption on the surface of activated carbon.
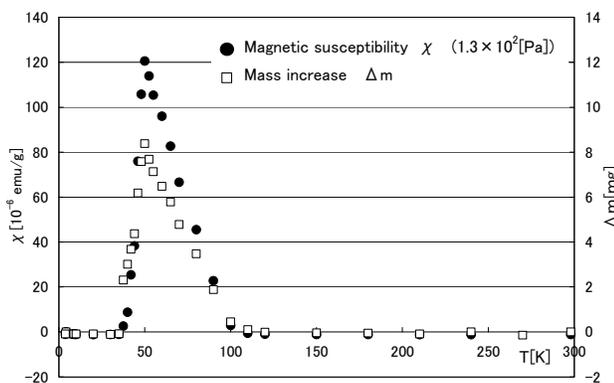

Figure (1) : Temperature dependence of magnetic susceptibility of bead-shaped activated carbon and mass increase.
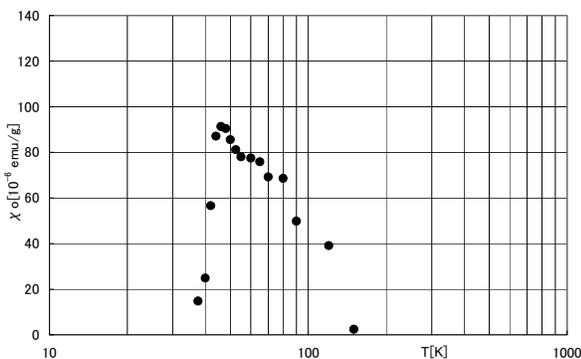

Figure (2) : Magnetic susceptibility of absorbed oxygen on the surface of bead-shaped activated carbon.
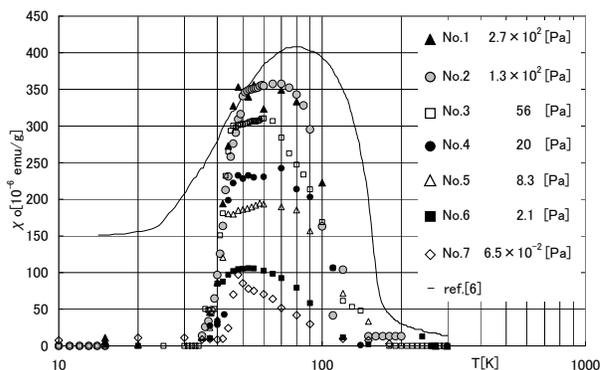

Figure (3) : Magnetic susceptibility of absorbed oxygen under various oxygen pressure for bead-shaped activated carbon.

Figure (1) also demonstrates variation of the specimen mass as a function of temperature, indicating that variation of the susceptibility corresponds well to that of the mass. This implies that the specimen mass increase with the oxygen adsorption and the observed susceptibility is a superposition of two components : activated carbon and oxygen. The susceptibility of the adsorbed oxygen can be evaluated by the following equation :

$$(m_o + m_c)\, \chi = m_o\, \chi_o + m_c\, \chi_c \qquad \text{---------(1)}$$

where m_o (= Δm) and m_c denote mass of adsorbed oxygen and activated carbon respectively, and χ_o and χ_c are the susceptibilities of adsorbed oxygen and activated carbon, respectively. Here, χ_c is estimated to be -1.0×10^{-6} emu/g.

Figure (2) illustrates temperature dependence of the magnetic susceptibility of adsorbed oxygen molecules evaluated from the above equation. The result indicates that the susceptibility increases sharply at around 40 K with an increase in temperature and exhibits a peak at about 50 K. The susceptibility becomes almost zero at above 150 K. The value of the susceptibility peak is about 10^{-4} emu/g.

Figure (3) shows temperature dependence of the susceptibility of adsorbed oxygen between 4.2 K and 300 K under various oxygen pressures. The magnitude of the oxygen susceptibility increases with an increase in the pressure up to 1.6×10^{2} Pa and then appears to reach a saturated value. The solid line in Figure (3) indicates the experimental result obtained for a one-dimensional oxygen array [6]. The magnitude of the peak for the one-dimensional array is similar to the maximum value for the adsorbed oxygen in the present work. Although the peak for the one-dimensional array is wider than those in the present work, the temperature dependence for the one-dimensional array is similar to those for specimens No.1 and No.2 in Figure (3) above 50 K. Kitaura and his coworkers have concluded that the one-dimensional oxygen array forms an antiferromagnetic state [6]. The present result also implies that the adsorbed oxygen molecules form an antiferromagnetic state. However, the structure of the adsorbed oxygen is not considered to be one-dimensional, because the formation of a one-dimensional oxygen array needs specially prepared molecular channels to

accommodate oxygen arrays [6], and the surface of activated carbon does not posses such a structure. In other words, micropores in activated carbon are not aligned along a certain direction but are distributed randomly on the surface. Therefore, adsorption of oxygen on the surface of activated carbon takes place two-dimensionally at an early stage and it becomes three-dimensional after oxygen layer reaches a critical thickness.
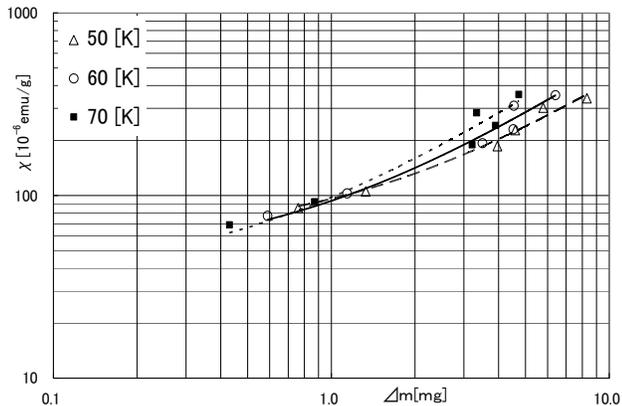

Figure (4) : Relation between magnetic susceptibility of oxygen and oxygen mass for bead-shaped activated carbon.
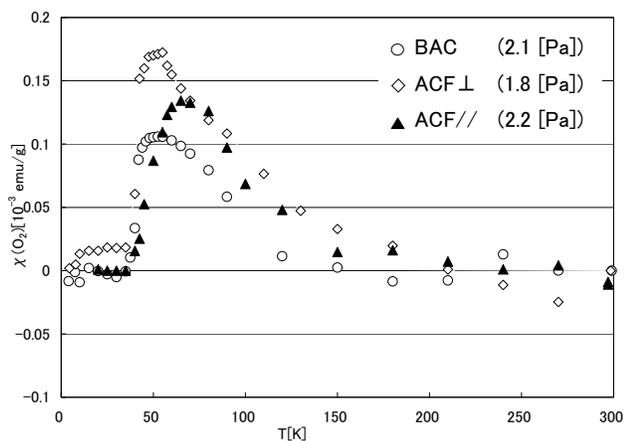

Figure (5) : Temperature dependence of magnetic susceptibility of absorbed oxygen on the surface of activated carbon fibers   measured in perpendicular ( ) and parallel (//) to the fiber axis with reference to that of bead-shaped activated carbon (BAC).

Figure (4) shows the relation between the magnetic susceptibility and the mass of adsorbed oxygen at 50, 60 and 70 K respectively. If the structure adsorbed oxygen is three-dimensional, the magnetic susceptibility should not depend on its mass at a constant temperature. However, the susceptibility increases with an increase in the mass. This result suggests that the structure of adsorbed oxygen is not three-dimensional but two-dimensional. It is considered that three layers of oxygen molecules exhibit the characteristics of a three-dimensional structure [7].
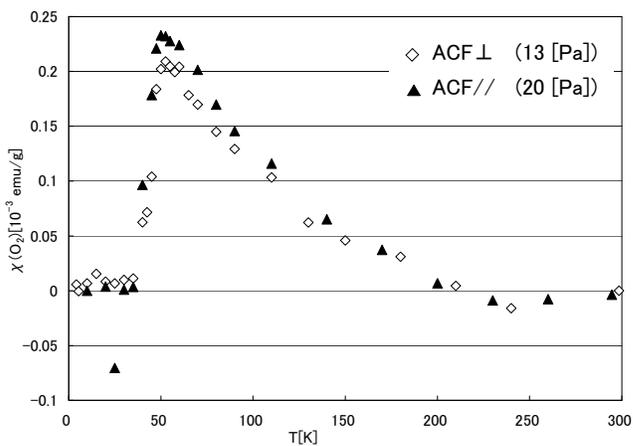

Figure (6) : Temperature dependence of magnetic susceptibility of absorbed oxygen on the surface of activated carbon fibers measured in perpendicular ( ) and parallel (//) to the fiber axis.
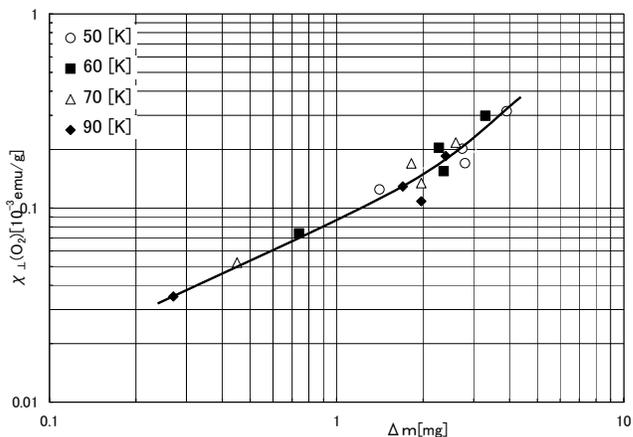

Figure (7) : Relation between the mass of absorbed oxygen and the magnetic susceptibility of absorbed oxygen measured in perpendicular to the fiber axis (χ).
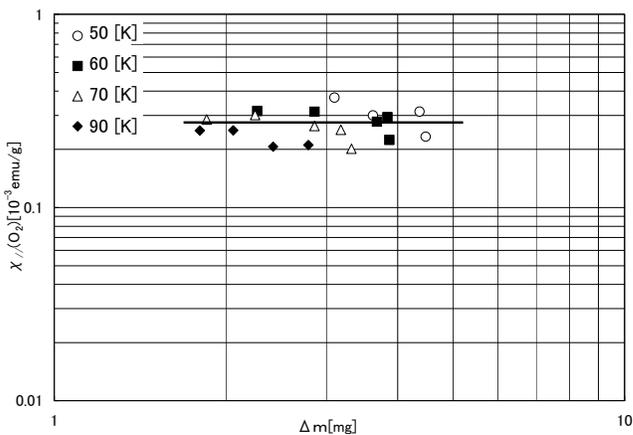

Figure (8) : Magnetic susceptibility of absorbed oxygen measured in parallel to the fiber axis ($\chi_{//}$) against mass of the absorbed oxygen.

Therefore, oxygen molecules adsorbed on the surface of bead-shaped activated carbon seem to form a thin film having less than three layers. Figure (4) shows that χ is approximately proportional to $\Delta m^{1/3}$ on an empirical basis. An important physical parameter to describe adsorption is the coverage, which is defined as the ratio of the adsorbate particle density to the substrate particle density [8]. The coverage in the present work should increase with an increase in Δm. However, it is difficult to obtain an exact relation between the coverage and Δm for such a defective surface as that of activated carbon.

Similar measurements of the susceptibility were carried out for activated carbon fibers under various oxygen pressures controlled at room temperature. The susceptibility was measured in both perpendicular and parallel to the fiber axis. Figure (5) shows temperature dependence of the magnetic susceptibility of adsorbed oxygen on the surface of activated carbon fibers measured in the above mentioned both directions under relatively low oxygen pressures. The result for bead-shaped activated carbon measured under similar oxygen pressure is also illustrated for comparison. It is readily seen that the susceptibility peak for carbon fibers measured in parallel to the fiber axis is observed at about 70 K, which is clearly higher than 50 K for bead-shaped activated carbon as well as activated carbon fibers measured in perpendicular to the fiber axis. This difference in the peak position could be resulted from the magnetic anisotropy of adsorbed oxygen between the both directions.

This difference in the peak position disappears with an increase in the oxygen pressure. Figure (6) illustrates similar results for carbon fibers obtained under oxygen pressure of one order magnitude higher than those shown in figure (5).The result for bead-shaped activated carbon is not shown in this figure for clearness. A significant difference in the peak position is not observed in this figure. Therefore, the magnetic anisotropy of adsorbed oxygen on the surface of activated carbon fibers between the two directions seems to be observed more clearly under lower oxygen pressure.

Figure (7) shows the relation between the adsorption mass (Δm) and the susceptibility of adsorbed oxygen measured in perpendicular to the fiber axis. This result is quite similar to that shown in figure (4) for bead-shaped activated carbon, implying that the structure of the adsorbed oxygen is two-dimensional and the thickness of thin film of oxygen molecules on the surface of activated carbon fibers is less than three layers in perpendicular to the fiber axis.

Figure (8) demonstrates the relation between Δm and the susceptibility of adsorbed oxygen on the surface of activated carbon fibers measured in parallel to the fiber axis. On the contrary to the results shown in figure (4) and figure (7), the susceptibility is constant against Δm. This result indicates that the adsorbed oxygen layer is sufficiently thick to regard it as three-dimensional along the fiber axis. This is reasonable if one imagines a thin cylindrical sheath made of oxygen molecules surrounding a bundle of carbon fibers. The thickness of the sheath is thin enough to regard it as a two-dimensional structure in perpendicular to the fiber axis but thick enough along the fiber axis to consider a three-dimensional structure. This discrepancy of Δm versus χ relation between the two directions suggests the structural and dimensional anisotropy of adsorbed oxygen molecules. This could be responsible for the difference in the peak position of χ versus T diagram shown in figure (5).

A more detailed study is needed for the elucidation of magnetic anisotropy of adsorbed oxygen in perpendicular and parallel to the fiber axis, which should reflect the difference in dimensionality of oxygen magnetism. In addition, theoretical work is also desired on the relation between magnetic susceptibility and coverage. The susceptibility-coverage relation has not been determined at present even for an oxygen monolayer adsorbed on a clean surface of highly crystalline graphite [9 - 13]. The experimental results shown in figure (4) and figure (7) should have theoretical reasons on the basis of the coverage-susceptibility relation. This is an issue to be studied in near future.

3. Summary and Conclusions :

The magnetic susceptibilities of bead-shaped activated carbon and activated carbon fibers were measured as a function of temperature between 4.2 K and 300 K under various oxygen pressures. The magnetic susceptibility exhibited a sharp peak at around 50 K. The positive peak was concluded to be due to the adsorption of oxygen on the surface of activated carbon. The magnetic susceptibility of the adsorbed oxygen was evaluated as a function of temperature from the experimental results, implying that the adsorbed oxygen formed an antiferromagnetic state. The relation between the susceptibility and the mass of adsorbed oxygen revealed that thickness of the adsorbed oxygen is thin enough to consider a two-dimensional structure for bead-shaped activated carbon and carbon fibers in perpendicular to the fiber axis but thick enough to regard it as a three-dimensional structure for carbon fibers in parallel to the fiber axis.

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