Effect of varying the ratio of matrix/dispersoid particle size on the piezoresistivity of alumina/carbon-black composite ceramics

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Revised; 8 April, 2011

Abstract

Alumina/carbon-black composite ceramics with different percolation thresholds were fabricated by changing the size ratio of constituent particles. The dependence of resistivity on pressure was established for each sample. The compositional dependence of resistivity can be explained by percolation theory. The percolation threshold decreases with increasing alumina/carbon-black particle size ratio. The pressure dependence of the resistivity increases as the composition approaches the percolation threshold. When the relative composition at the percolation threshold is fixed, the sensitivity increases with increasing matrix/dispersoid initial particle size ratio.

Kewwords: percolation, piezoresistivity, pressure sensor, particle size

1. Introduction

When the volume fraction of electrically conductive particles increases in an insulating matrix, the material changes from being an insulator to being a conductor [1, 2, 3]. This phenomenon is known as the percolation transition. The composition (volume fraction of particles) at the percolation transition is called the percolation threshold. Near the percolation threshold, the electrical conductivity changes exponentially [2, 3]. In addition to the basic research reported here, an application to sensing devices for environmental changes has also been considered: changes in temperature and applied load effect changes in composition [4-14].

One of the authors has developed a pressure and temperature sensor based on polymer matrix/conductive inorganic filler composites [4, 5, 6]. We have also evaluated a pressure sensor utilizing dielectric ceramic matrix/carbon particle composites [7, 8]. The former is based on two-dimensional, and the latter is based on three-dimensional percolation transitions.

Pressure sensors for use at high temperatures should be constituted of only inorganic components having good heat and corrosion resistance. In general, inorganic insulators have large elastic moduli or experience small volume changes on the application of loads. As a result, any compositional change of insulator matrix/conductor dispersoids composite is small and leads to only a small change in resistivity per unit load (piezoresistivity effect).

We have previously reported a sensitivity enhancement in graphite dispersed composites based on alumina or magnesia matrix by setting the composition at the percolation threshold. These results provided the basis for making a pressure sensor based on the percolation transition phenomenon [7, 8].

The percolation threshold is known to depend on the particle size ratio [15] and morphology of the electrical conductive dispersoids [16, 17]. The effects of these on the sensitivity of a pressure sensor, however, have not been systematically investigated. In the present study, composite ceramics having different percolation thresholds were fabricated by changing the size ratio of the insulator matrix/conductor dispersoid particles. The pressure dependence of resistivity was measured for each sample. To evaluate the compositional dependency of the sensitivity, the respective compositions were normalized by the percolation threshold for each constituent particle size ratio. Based on these investigations, the most favorable particle size ratio in the pressure sensor based on the percolation transition is discussed from a technological point of view.

2. Experimental procedure

Composite ceramics were fabricated that were composed of electrically conductive/insulator phases having different initial powder particle size ratios. Electrical resistivity was measured on these various composites under applied loads.

Two kinds of carbon black and three kinds of alumina were used to make six sets of powder mixtures with different *D/d* ratios, where *d* and *D* are the average particle sizes of carbon black and alumina, respectively. Fine carbon-black particles having sizes of 24 nm and 55 nm (MC100:MC220, Mitsubishi Chemical, Tokyo, Japan) were dispersed into the alumina base powder having an average diameter of 300 nm, 500 nm (AKP-30:AKP-20, Sumitomo Chemical, Tokyo, Japan), or 1000 nm (Guaranteed grade, Koujundo Chemical, Tokyo, Japan). The resultant *D/d* values for the six sets of powder mixtures were 5.5, 9.5, 12.5, 18.2, 20.8, and 41.7. The volume fraction of carbon black was varied in each group of powder mixtures.

Both carbon-black and alumina powders were weighed to make the desired weight ratios in each group. The powders were ball milled with ethanol for one hour by a planetary ball mill (P-6, Fritsch, Germany) in a polyethylene bottle and then dried. The resultant powder mixtures were uniaxially pressed at 20 MPa in a steel die having a diameter of 14 mm, followed by cold isostatic pressing (100 MPa) and transfer to a graphite die for hot pressing. The hot pressing was conducted under argon atmosphere with a uniaxial pressure of 28 MPa at 1500 ^{o}C for 1 h. Densities were measured by the Archimedes method using water as a medium. Microstructures were observed by SEM on fracture surfaces.

The obtained sintered bodies had relative densities of 90–95% of the theoretical value calculated from the composition and constituent densities. The carbon-black volume fraction (x) was calculated from the measured density (Pm) and weight fraction of carbon black (w_{CB}) per our previous studies [7,8].

Rectangular specimens with dimension of 6 x 5 x 3 mm^3 were cut from the pellets for resistivity measurement with and without applied loads. Platinum electrodes were sputtered onto each 5 x 3-mm^2 face, and the resistance between the two faces was measured. Uniaxial compressive load was applied on a sample sandwiched between yttria-stabilized zirconia insulating plates using an autograph (EZ-graph, Shimazu, Kyoto, Japan). As the load was applied between the 6 x 5-mm^2 faces, the direction of the applied stress was perpendicular to the electrical current.

3. Results and discussion

Figure 1 illustrates the resistivities of alumina/carbon-black composite ceramics with various ratios of matrix/dispersoid particle size as a function of the carbon-black volume fraction, x. In all samples, the resistivity decreased rapidly with increasing x. Such behavior can be explained by percolation theory. Based on this theory, there is a critical concentration or percolation threshold (x_c) at which a conductive path is formed, causing the composite insulator to conduct. When x approaches x_c, the resistivity ρ can be written as,

$$\rho = \rho_0 (x - x_c)^{-t} \quad (x > x_c), \qquad (1)$$

where ρ_0 is a prefactor, and t is the critical exponent for the resistivity.

Through a nonlinear fit of Eq. (1), both x_c and t were obtained for the six sets of composites having different D/d and x_c. The results are plotted in Fig. 2(a) together with t. The data are classified into two groups as represented by the two straight lines in the figure. In both groups, x_c decreases with increasing D/d value. The values of t were almost constant, ranging from 1.7 to 1.9 irrespective of the D/d value.

Such D/d dependence of x_c has already been reported by Kusy [15] and explained theoretically. In the present study D/d values all exceed 5, resulting in smaller x_c values than theoretical (x_c = 0.18) values for composites having equal D and d sizes (D/d = 1). Differences between this research and the work of Kusy [15] could derive from the starting powder, i.e., the composites made from larger alumina particles should have higher percolation thresholds. A possible reason is the difference in particle parameters; that is, in the present study we used the size ratio of the starting powder, whereas Kusy used that of the final product [15]. The size ratio in the final product might differ from that for the starting mixture due to the mixing process and sintering process.

The particle size ratios of the final products were obtained from observations of the microstructures. The percolation thresholds are re-plotted against *D/d* (final) in Fig. 2(b). Hereafter, the particle size ratios of the final products *D/d* (final) is distinguished from the previously used one *D/d* (initial). Since no compositional dependence can be seen in *D/d* (final), it is determined to be a unique value for a set of alumina/carbon black combination. Unlike Fig. 2(a), where the data are plotted against *D/d*(initial), plots against *D/d* (final) form a single curve irrespective of the kinds of starting powder. In the present case, the percolation thresholds decreased monotonically with *D/d* (final) which accords with that reported by Kusy [15]. He explained such dependency in connection with the surface fraction of larger particle.

Figure 3 shows the typical pressure dependence of the resistance for the sample after several loading and unloading cycles. For all samples, the resistance decreased linearly with increasing applied pressure. As shown in Fig. 3, there was excellent reproducibility of the data between loading and unloading. The solid line is the linear fit to the data. The normalized pressure coefficients of the resistance, d(ln *R*)/d*P*, or sensitivity, were obtained from the slope of the linear fits. The resulting d(ln *R*)/d*P* values are all negative, - d(ln *R*)/d*P* are plotted in Fig. 4(a) as a function of *D/d* (initial) for x = 1.15 x_c, 1.5 x_c, and 2.0 x_c.

In any samples having different particle size ratios, - d(ln *R*)/d*P* are in the order 1.15 x_c > 1.5 x_c > 2.0 x_c. For a given x_c value, on the other hand, - d(ln *R*)/d*P* tends to increase with increasing *D/d* (initial) value. In other words, the smaller the x_c is, the larger the - d(ln *R*)/d*P* value becomes.

The particle size ratio dependence of the percolation threshold is closely related to *D/d* (final) rather than *D/d* (initial). Then, *D/d* (final) is taken as the abscissa and re-plotted in Fig. 4(b). Contrary to the percolation threshold, the sensitivity greatly depends on *D/d* (initial) rather than on *D/d* (final).

For uniaxial pressure applied perpendicularly to the direction of the current, the pressure coefficient of the resistance is expressed as [8]

$$\frac{d(\ln R)}{dP} = \frac{d(\ln \rho_F)}{dP} + \frac{t}{x - x_c}\frac{x(1-2\gamma)}{E} + \frac{1}{E}, \qquad (3)$$

where *E* is Young’s modulus, and γ is Poisson’s ratio.

The first and last terms in Eq. (3) have no *x* dependence, and the observed increase in

|d(ln R)/dP| can be explained by a strong enhancement in the second term as the carbon-black content approaches x_c [7, 8].

When a fixed value relative to x_c is substituted for x in Eq. (3), for example $x = 1.5\ x_c$, the sensitivity d(ln R)/dP becomes independent of x_c. The sensitivity dependence of x_c on initial *D/d* cannot be explained by this equation. Other parameters not included in this equation could affect the dependence of sensitivity on particle size ratio. One such factor could be differences in the homogeneity of the dispersions between samples, as the sensitivity depends strongly on the initial size ratio and only slightly on the final size ratio. Further studies are needed to explore this concept.

4. Conclusions

The present study has demonstrated that the sensitivity increases with increased matrix/dispersoid initial particle size ratio when the composition relative to the percolation threshold is fixed. Based on our previous work, we conclude that the sensitivity would be improved by using insulator/conductor particles having larger size ratios and compositions near the percolation thresholds.

Because sinterability tends to decrease when certain hetero materials are introduced, small loadings of electrically conductive materials using larger particle size ratios.

would be advantageous in fabrication. On the other hand, electrical resistivity becomes too large to measure as the percolation threshold is approached. The practical composition is limited to the measurable range of resistances.

Acknowledgements

This work was supported in part by Mitutoyo Association for Science and Technology (MAST).

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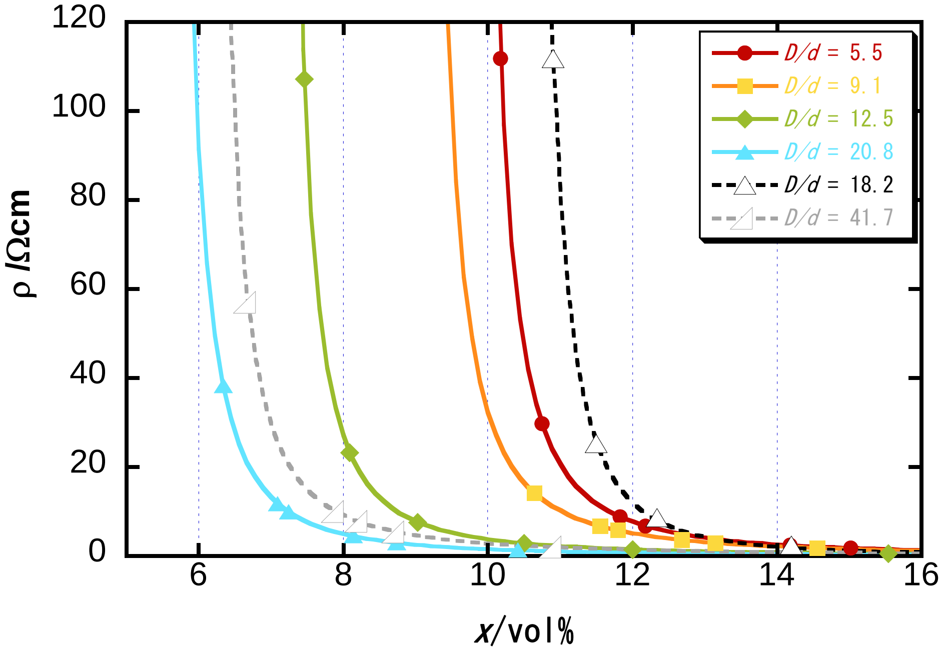
Figure Captions

Fig.1 Resistivity of alumina/ carbon black composites with various matrix /dispersoid initial particle size ratios (*D/d*) as a function of the carbon black volume fraction (x).

Fig.2 Percolation threshold (x_c) and critical exponent for the resistivity (t) as a function of matirix /dispersoid particle size ratio. Open symbols are derived from the largest alumina powder. Abscissa:(a)initial size ratio, (b)final size ratio.

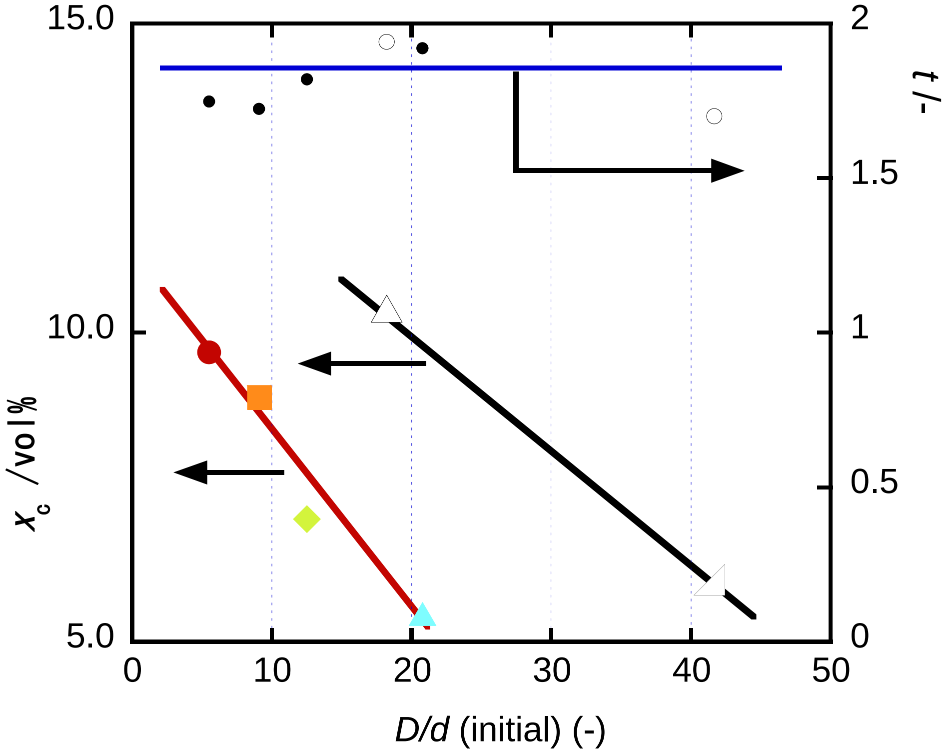
Fig.3 Representative pressure dependence of resistance (*D/d*(initial) =18.2, x = 10.9 vol%). Filled triangles and open triangles are for increasing and decreasing pressure.

Fig.4 Pressure Sensitivity as a function of matrix /dispersoid particle size ratio for three kinds of composition relative to percolation threshold (x_c). Triangle: $x = 1.15x_c$, Square: 1.5 x_c and Circle: 1.5 x_c. Open symbols are derived from the largest alumina powder. R^2:decision coefficient, Abscissa: (a)initial size ratio, (b)final size ratio.



120
100
80
60
40
20
0
ρ /Ωcm
6
8
10
12
14
16
x/vol%
D/d = 5.5
D/d = 9.1
D/d = 12.5
D/d = 20.8
D/d = 18.2
D/d = 41.7

Fig.1



15.0
10.0
5.0
2
1.5
1
0.5
0
t /-
x c /vol%
0
10
20
30
40
50
D/d (initial) (-)

Fig.2(a)

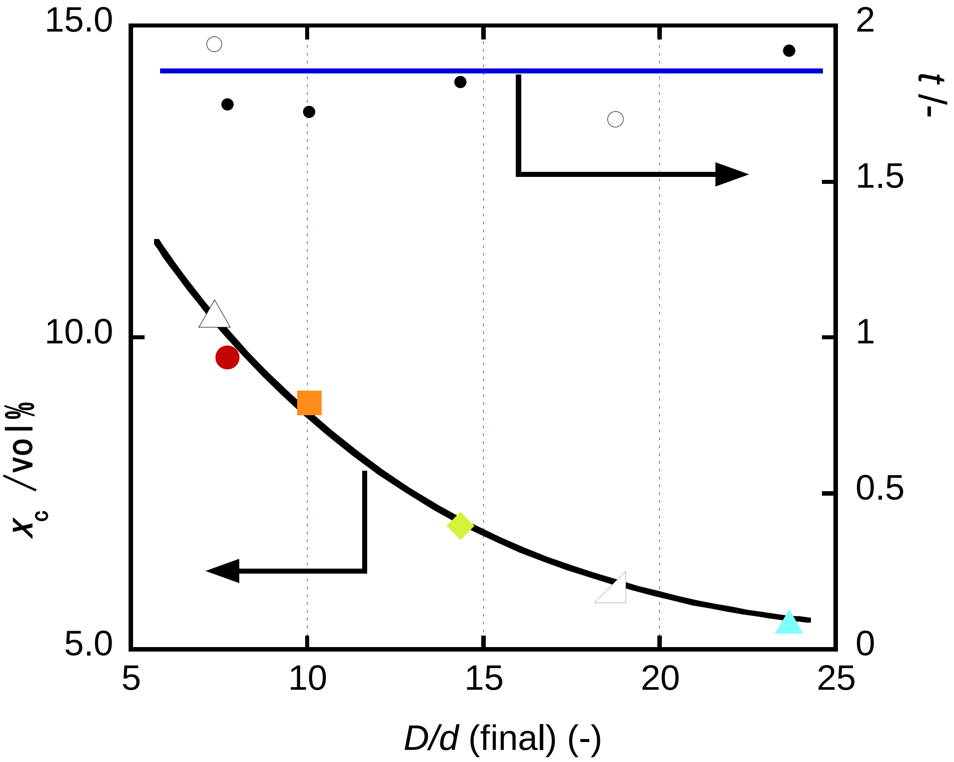

15.0
10.0
5.0
5
10
15
20
25
2
1.5
1
0.5
0
x_c /vol%
t /-
D/d (final) (-)

Fig.2(b)

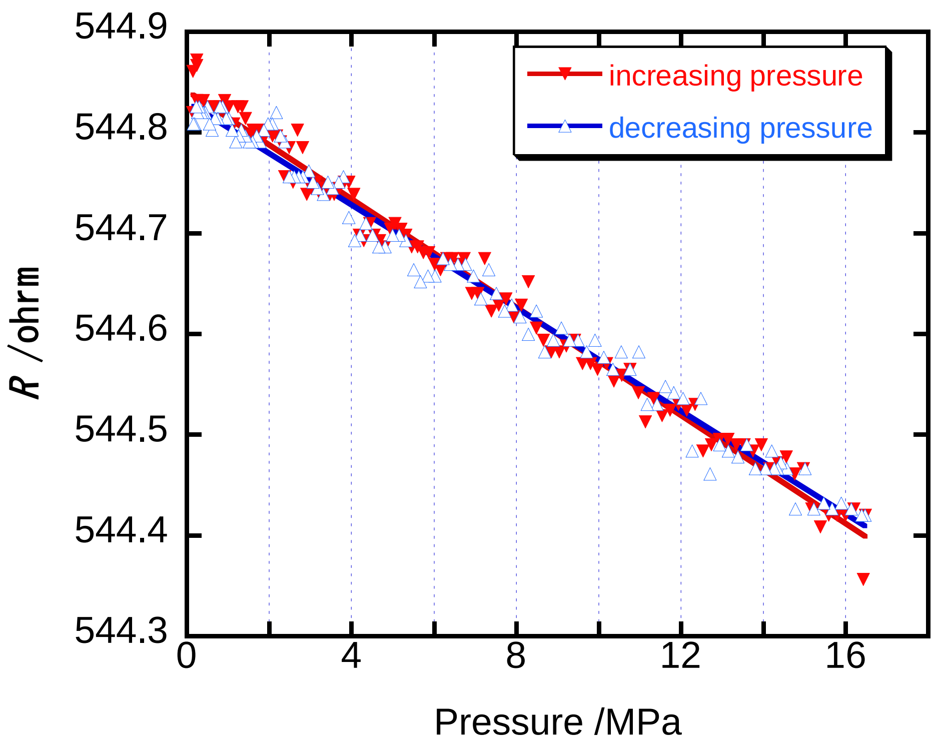
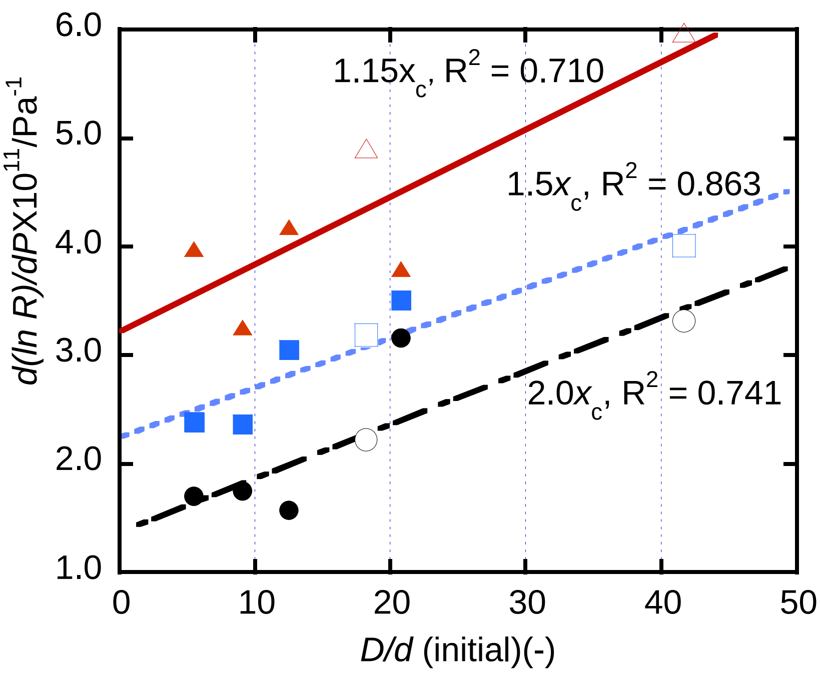
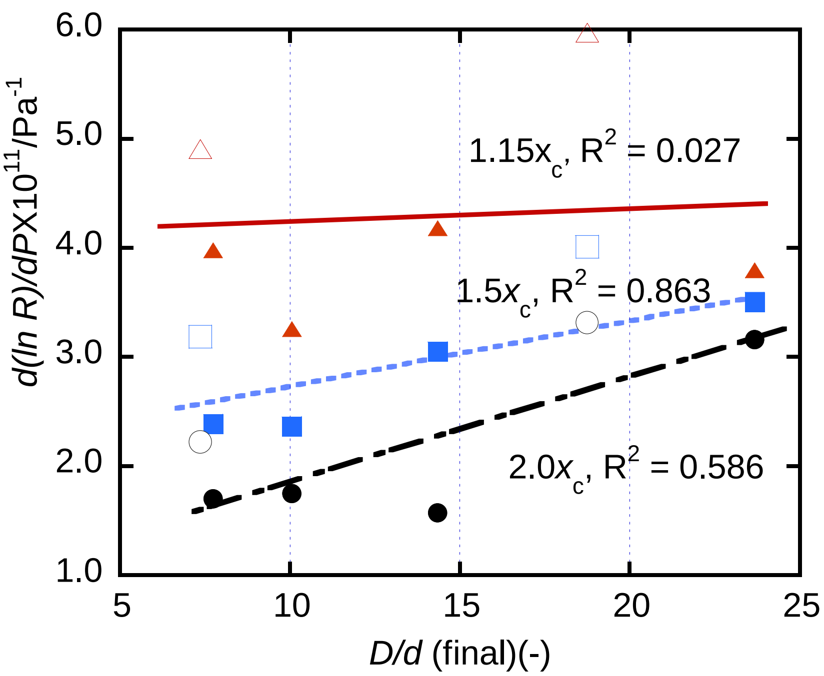

544.9
544.8
544.7
544.6
544.5
544.4
544.3
0
4
8
12
16
R /ohm
Pressure /MPa
increasing pressure
decreasing pressure

Fig.3



1.15x_c, R² = 0.710
1.5x_c, R² = 0.863
2.0x_c, R² = 0.741
d(ln R)/dPX10^11/Pa^-1
D/d (initial)(-)

Fig.4(a)



1.15x_c, R² = 0.027
1.5x_c, R² = 0.863
2.0x_c, R² = 0.586
d(ln R)/dPX10^11/Pa^-1
D/d (final)(-)

Fig.4(b)