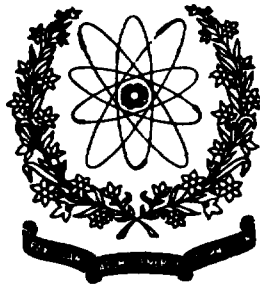


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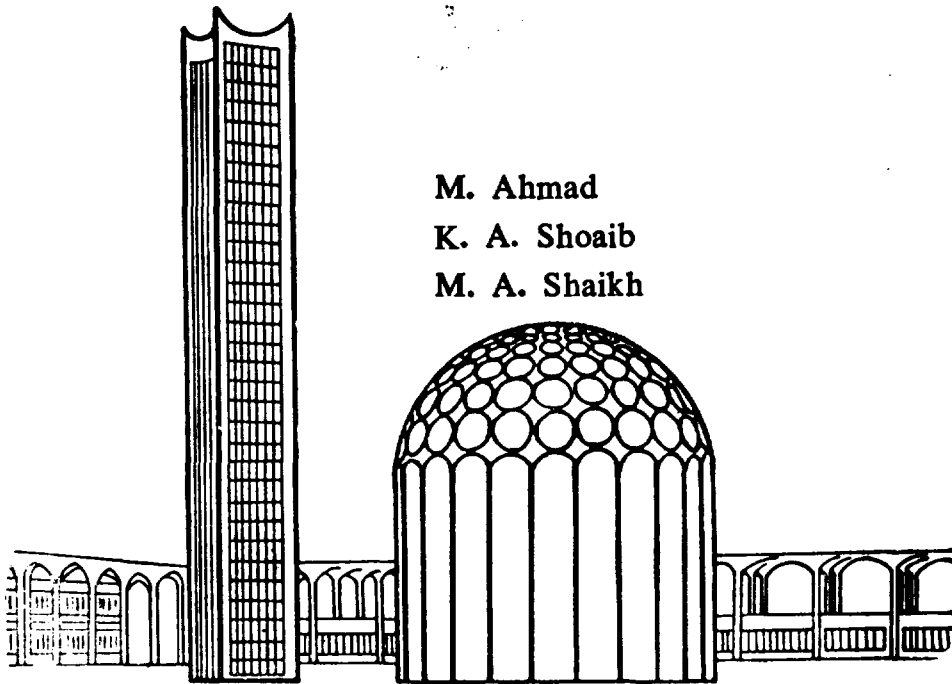
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# Study of Diffusivity of Sb and Si in DIN 1.6770 Ferritic Steel

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## ABSTRACT

*Diffusion coefficients of Sb and Si in  $2\frac{1}{4}$  Cr-1Mo-NiNb stabilized ferritic steel (DIN 1.6770) were determined from concentration profiles measured using energy dispersive x-ray microanalysis in the scanning electron microscope. Activation energies  $Q$  and frequency factor  $D_0$  was calculated for different ranges of temperature for Sb and Si. The values of diffusion coefficients of Sb were found to be higher than those of Si in this alloy.*

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## 1. INTRODUCTION

When certain alloy steels are held within, or cooled slowly through a certain temperature range, brittleness of the material occurs which is called temper embrittlement. Temper embrittlement has been recognized as an industrial problem in such steels for well over 50 years, but an understanding of its causes has begun only recently. Generally it is assumed that the segregation of trace elements or impurities, such as P, Sb, Sn and As to the grain boundaries induced temper embrittlement when the steels are held within the embrittling temperature range 370-570°C [1-3]. It has been stated that Sb segregation, in combination with its low melting points, is probably the only source of embrittlement in iron and steels during hot forming.

Third elements can influence the amount of segregation that occurs. For example, it has been well established that the amount of Sb at grain boundaries depends on the presence of Ni [4]. Both Mn and Si strongly promote phosphorus segregation, resulting in an increase in embrittlement susceptibility, whereas Mo plays a beneficial role up to a certain extent [5,6]. In addition, impurity segregation can also be influenced by rather complex interactions with other alloying elements, by involvement with precipitates [7] and possibly with lattice defects [8].

Many of the transformation processes occurring in the solid state, especially those involving precipitates, growth of second phases and segregation of trace elements or impurities to the grain boundaries [9] are diffusion-controlled. The availability of appropriate diffusion data can help in the interpretation of embrittlement kinetics and may, in some instances, highlight certain details of the embrittlement mechanisms.

One practical problem is that most diffusion data are obtained at high temperatures and this necessitates the extrapolation towards the lower temperature where embrittlement occurs. Furthermore, in high alloyed materials, volume diffusion coefficients have been shown to depend upon the actual composition of the alloys [10-12]. It is,

therefore, necessary to obtain diffusion data for each individual alloy of interest. The diffusion of Sb in steel is also of technical interest in view of Sb coating of steel to improve its corrosion resistance [13].

In this work the diffusivity of Sb and Si was studied in a  $2\frac{1}{4}$ Cr-1Mo ferritic steel, with the German denomination DIN 1.6770 which is Nb stabilized and contains small additions of Ni. The diffusion measurements were performed in the temperature regions of 475 to 600°C for Sb and diffusivity of Si was determined at 475°C and 800°C. Concentration gradient, measured using microprobe analyser (EPMA), was used to determine the diffusion coefficients for both the elements.

## **2. EXPERIMENTAL METHOD AND EVALUATION PROCEDURES**

### **2.1 Preparation of Specimens**

Chemical composition of the steel investigated is given in Table 1. The material was in the form of a sheet of dimension 500x15x3 mm, from which samples were cut to a size of 10x7x3 mm. The specimens were austenitized at 1150°C for 1, 5 and 24 h to investigate the influence of austenitization time on grain size. The grain size measurements were carried out and grain diameters of 50  $\mu$ m were determined for the samples heat treated at 1150°C for 24 h. The specimens were polished on three sides to get flat surfaces for the diffusion measurements.

Two methods were used to produce diffusion couples. In the first series, specimens were enclosed in quartz capsule filled with Sb or Si powder of 100 mesh. The capsules were evacuated up to  $1 \times 10^{-4}$  torr, filled with helium gas (99.999% purity) and sealed to prevent the specimens from oxidation. The specimens which were embedded in Sb powder were annealed for 120 h at 475 and 600°C. Those which were embedded in Si powder were annealed for 120 h at 475 and 800°C, respectively. A temperature variation of  $\pm 2^\circ\text{C}$  was recorded during the heat treatment. The capsules were quenched in cold water after diffusion-annealing. After heat-treatment nearly 1 mm of one of the polished surface was removed by grinding and was re-polished to reveal the two diffusion interfaces.

In the second series, specimens were prepared by vacuum evaporation of thin layers of Sb or Si on a well polished side of the specimen. The above mentioned process was adopted for polishing and for the prevention of oxidation of the specimens. These diffusion couples were annealed in the range of 550-600°C for Sb coated, and 475°C for the Si coated, specimens.

The diffusion couples produced by both methods were also etched to show the grains and concentration was measured across the interface of Si or of Sb with the largest grain of the steel.

## **2.2 Measurement of Concentration Gradients**

Measurement of the concentration gradient  $c(x)$  was carried out on the scanning electron microscope Philips SEM 505 attached with an EDAX energy dispersive spectrometer. All the data was taken at an accelerating voltage of 30 kV. The concentration profiles  $c(x)$  were then taken through the largest grain in steps of 1 or 1.5  $\mu\text{m}$  along the  $x$ -axis. The data was taken to the point where the concentration of Si or Sb reduced to zero. Concentration profiles were plotted as  $c(x)$  vs.  $x$  in Figs. 1-4 for infinite couples and as  $\log c(x)$  vs.  $x^2$  in figs. 5-7 for thin coated samples. These plots were then used to determine  $D$  as described below.

## **2.3 Evaluation of Diffusion Coefficients**

Multicomponent diffusion is usually expressed in terms of interdiffusion coefficients which determine the rate of material being transported along a given concentration gradient. One method for calculating diffusion coefficient in unidirectional diffusion is based on the solution of Ficks second law of diffusion

$$dc/dt = d/dx (D dc/dx) \quad (1)$$

where  $D$  is the diffusion coefficient or diffusivity,  
 $c$  is the concentration,  
 $x$  is distance normal to the interface,  
 $t$  is the time.

The application of this leads to the well known equation for the determination of the diffusion coefficients for infinite couples [14]

$$\frac{[c(x)-c(0)]}{[c(1)-c(0)]} = \frac{1}{2} \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \quad (2)$$

where  $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-y^2) dy$ ,  $c(x)$  is the concentration of solute at  $x$ .  $c(0)$  is the concentration of the solute at  $x < 0$ ,  $c(1)$  is the concentration of the solvent at  $x \gg 0$  and interface of the diffusion couples lies at  $x=0$ . For the evaluation of  $D$  those ranges in Figs. 1-4 were taken in the region where the concentration  $c(x)$  of the solute varies linearly with the distance  $x$ .

Also, using eq.(1), the expression for the measurement of diffusion coefficient of diffusion couples prepared by coating thin film is;

$$c(x) = \frac{\text{Const.}}{2\sqrt{\pi Dt}} \exp. \left[ -\frac{x^2}{4Dt} \right] \quad (3)$$

By plotting for a given time the  $\log c(x)$  values versus  $x^2$  the  $D$  value can be calculated by determining the slope of the straight lines in Figs. 5-7.

### 3. RESULTS AND DISCUSSION

#### 3.1 Diffusion Coefficients

The diffusion coefficients  $D$  of Sb and Si in the steel, determined for the particular annealing conditions, are given in Table 2. Where a direct comparison is possible the  $D$  values determined with infinite couples are slightly higher than that for thin film coated specimens. Also, we can state that the diffusivity of Sb is higher than that of Si for the temperature investigated. The values of the diffusion coefficients are increasing with the increase of temperature for both Sb and Si. This conforms to the general phenomenon that the diffusivity increases with increasing temperature.



### 3.2 Activation Energy Q and Frequency Factor D<sub>0</sub>

The values of the activation energies for the diffusion of Sb and Si in 1.6770 steel were calculated using the relation

$$\log (D_1/D_2) = -Q/R (1/T_1-1/T_2) \quad (4)$$

where  $D_1$  is the diffusion coefficient at temperature  $T_1$ ,  $D_2$  is the diffusion coefficient at temperature  $T_2$  and  $Q$  is the activation energy. The frequency factor  $D_0$ , a constant in the well known Arrhenius equation, which is a relation between reaction rate and absolute temperature, was calculated for both Si and Sb by plotting  $\log D$  vs.  $1/T$  and extrapolating the curve to  $T=0$ . The calculated values of  $D_0$  and  $Q$  are given in Table 3.

In Fig. 8 the experimentally determined diffusion data are plotted for Sb and Si as a function of  $1/T$ . In addition, the already published data [15,16] on the diffusivity of both elements in  $\alpha$ -Fe are extrapolated down to the temperature range of interest, i.e. to 475°C. The published diffusion coefficients of Sb in a dilute Fe-0.69 at% Sb alloy [17] are also included in Fig.8. As can be seen from the figure the already reported values of activation energy for both the elements are higher in  $\alpha$ -Fe than the values measured in 1.6770 steel is different from the diffusivity of Si in  $\alpha$ -Fe. Two activation energies were obtained for Sb in 1.6770 steel. The values of  $Q$  are 1.3eV between 475 and 600°C (infinite couple) and 2.3eV between 550 and 600°C (thin coated specimens). The diffusivity of Sb in 1.6770 steel is very much higher than that in  $\alpha$ -Fe at lower temperature (temper embrittlement range). The deviation in diffusivity of the order of one magnitude can be explained on the basis of difference in concentration gradient of Sb at lower temperature. According to Nishida et al [15] the value of diffusivity changes much with higher concentration gradient at lower temperature than that at higher temperature. In the present study the difference in concentration gradient is expected because of application of different technique.

## SUMMARY

1. Diffusion coefficients of Si and Sb have been measured in the temperature range 475-600°C, while the diffusivity of Si has been determined at 475 and 800°C.
2. The measured value of diffusivity at the temperature of maximum embrittlement (475°C) is higher than that expected from low temperature extrapolation of diffusivity data in  $\alpha$ -Fe. In the temperature range 550 to 600°C (using thin coated specimens) the measured diffusivity data are comparable with extrapolated high temperature diffusivity of Sb in  $\alpha$ -Fe.
3. Antimony diffuses faster in 1.6770 than silicon. Both elements are known to behave as fast diffusing elements.
4. The activation energy determined for Sb by using infinite couple samples in the temperature region 475-600°C is lower than the value determined by using the thin coated samples in the temperature region 550-600°C.

## ACKNOWLEDGEMENTS

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## FIGURE CAPTIONS

- Fig.1. Variation of Sb concentration (c) vs. diffusion distance (x) at 475°C.
- Fig.2. Variation of Sb concentration (c) vs. diffusion distance (x) at 600°C.
- Fig.3. Variation of Si concentration (c) vs. diffusion distance (x) at 475°C.
- Fig.4. Variation of Si concentration (c) vs. diffusion distance (x) at 800°C.
- Fig.5. Log of Sb concentration (c) vs. square of diffusion distance ( $x^2$ ) at 550°C.
- Fig.6. Log of Sb concentration (c) vs. square of diffusion distance ( $x^2$ ) at 600°C.
- Fig.7. Log of Si concentration vs. square of diffusion distance ( $x^2$ ) at 475°C.
- Fig.8. Diffusion Coefficients D vs.  $1/T$ .

Table 1: Chemical composition of the  $2\frac{1}{4}$  Cr-1Mo-NiNb stabilized steel (DIN 1.6770).

Element	Wt. %	Element	Wt. %
C	0.063	P	0.012
Si	0.27	S	0.008
Mn	0.65	N	0.009
Cr	2.42	Co	0.011
Ni	0.51	Ta	0.01
Mo	1.00	B	<10 ppm
Nb	0.78		

Table 2: Measured diffusion coefficients for Si and Sb in the steel.

Solute	Temperature °C	Annealing Time hours	$D$ [m <sup>2</sup> /sec]	Couples
Si	475±2	120	$1.2 \times 10^{-18}$	infinite
Si	475±2	240	$1.0 \times 10^{-18}$	thin film
Si	800±2	120	$1.3 \times 10^{-16}$	infinite
Sb	475±2	120	$2.2 \times 10^{-18}$	infinite
Sb	550±2	120	$6.25 \times 10^{-18}$	thin film
Sb	600±2	120	$4.0 \times 10^{-17}$	infinite
Sb	600±2	120	$3.5 \times 10^{-17}$	thin film

Table 3: Calculated frequency factor  $D_0$  and activation energies  $Q$  for Sb and Si in the alloy.

Solute	Temperature range [°C]	$D_0$ [m <sup>2</sup> /sec]	$Q$ [ev]
Si	475-800	$3.4 \times 10^{-12}$	1.0
Sb	475-600	$3 \times 10^{-9}$	1.3
Sb	550-600	$6.6 \times 10^{-4}$	2.3

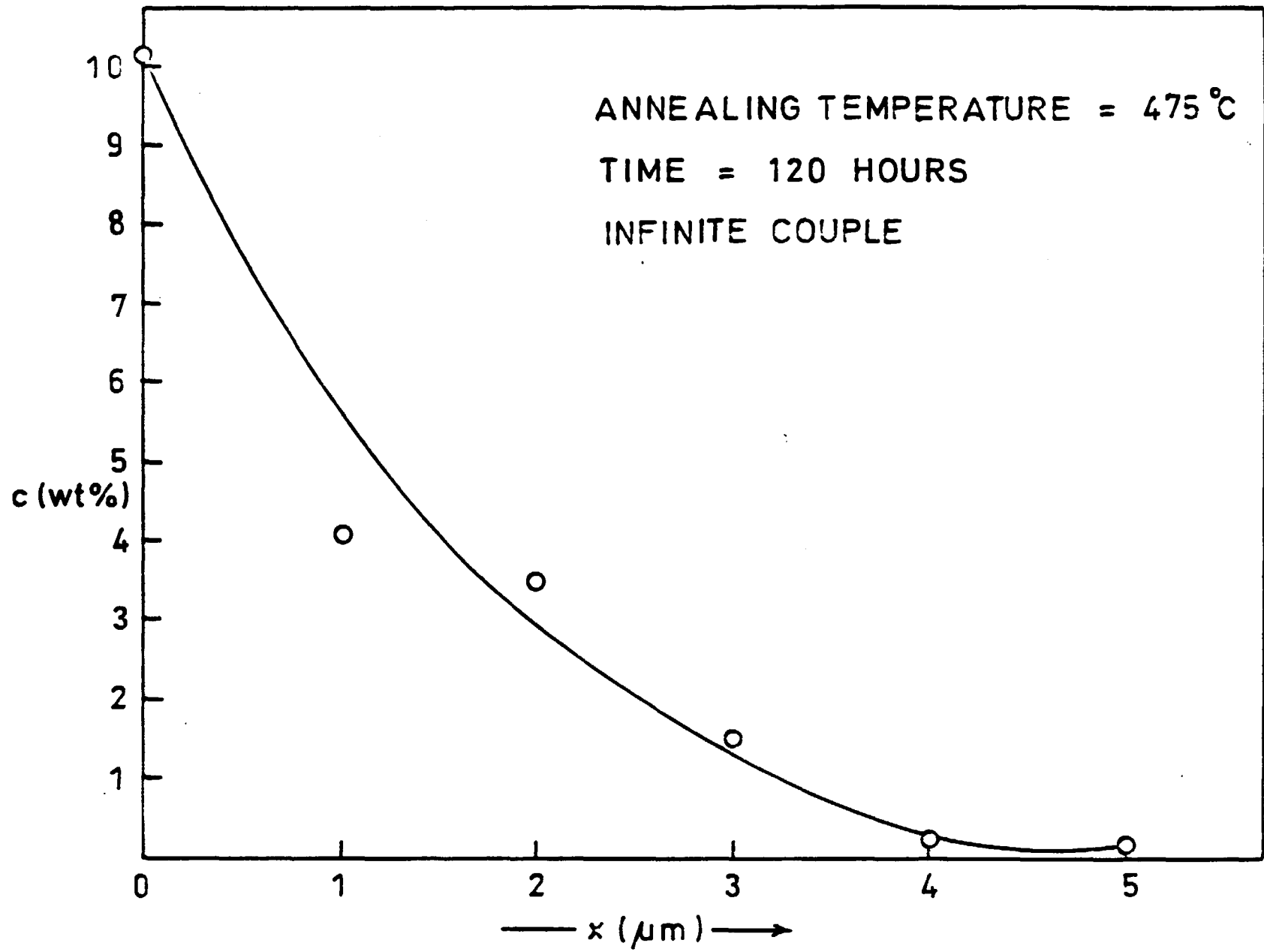


Fig.1

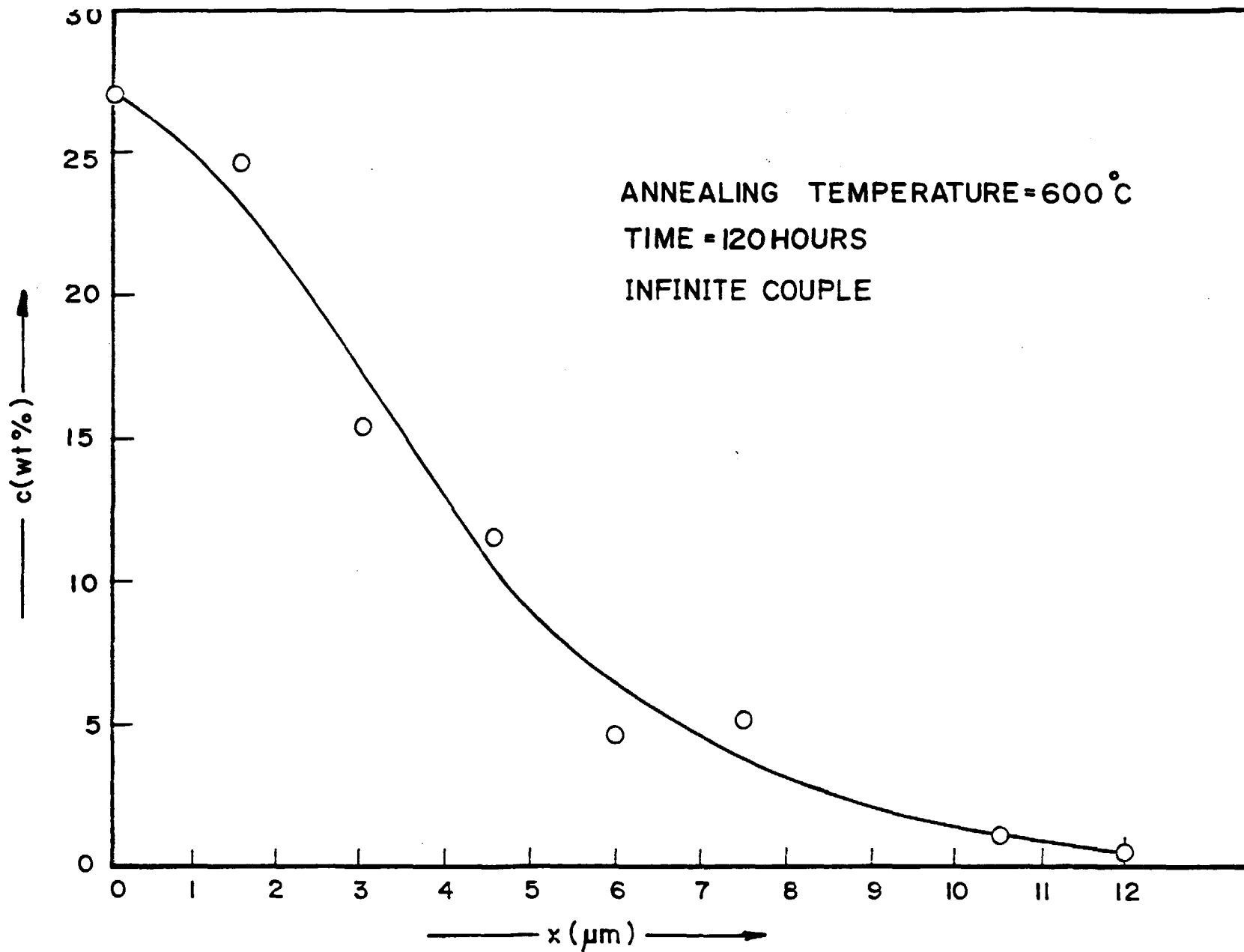


Fig.2

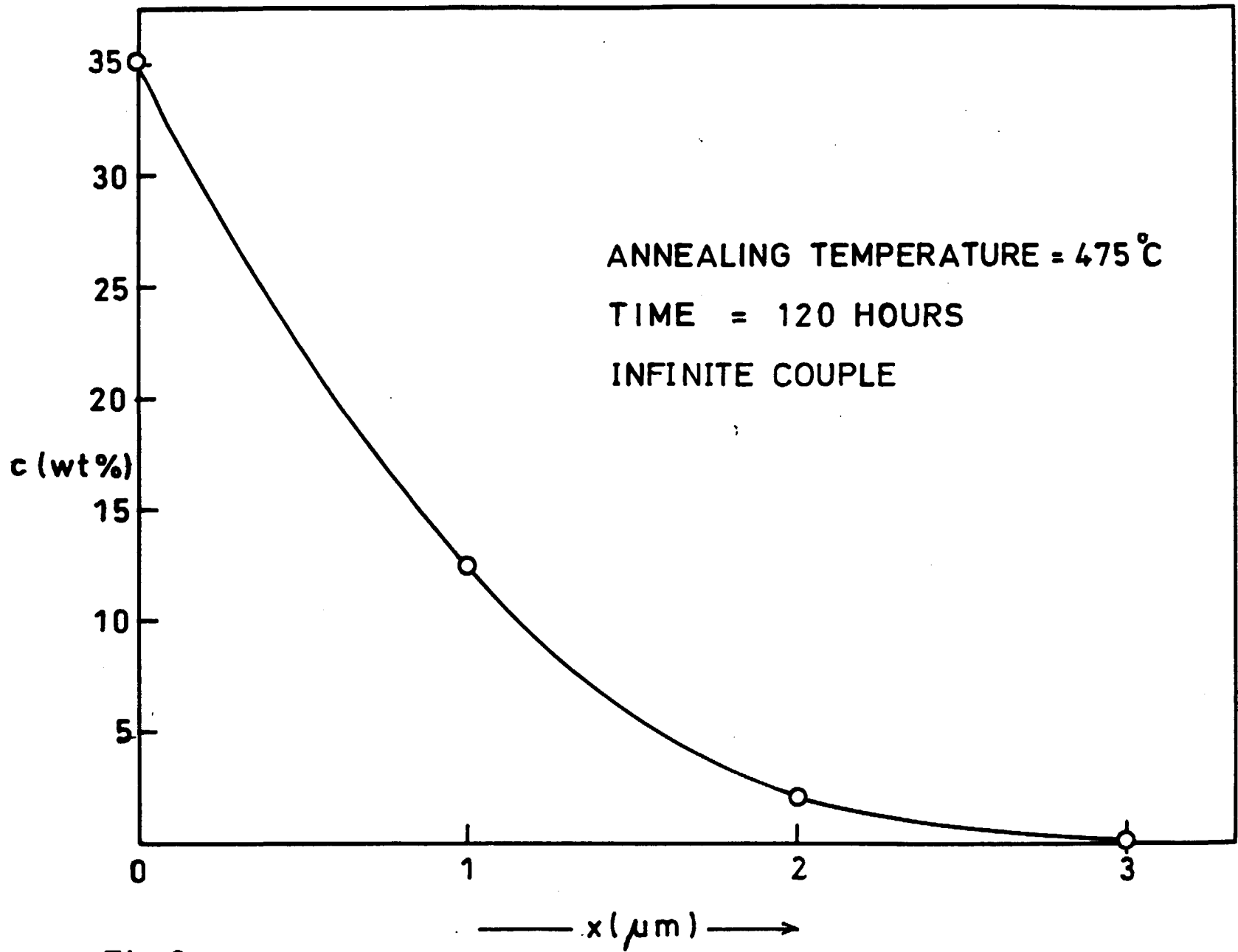


Fig. 3



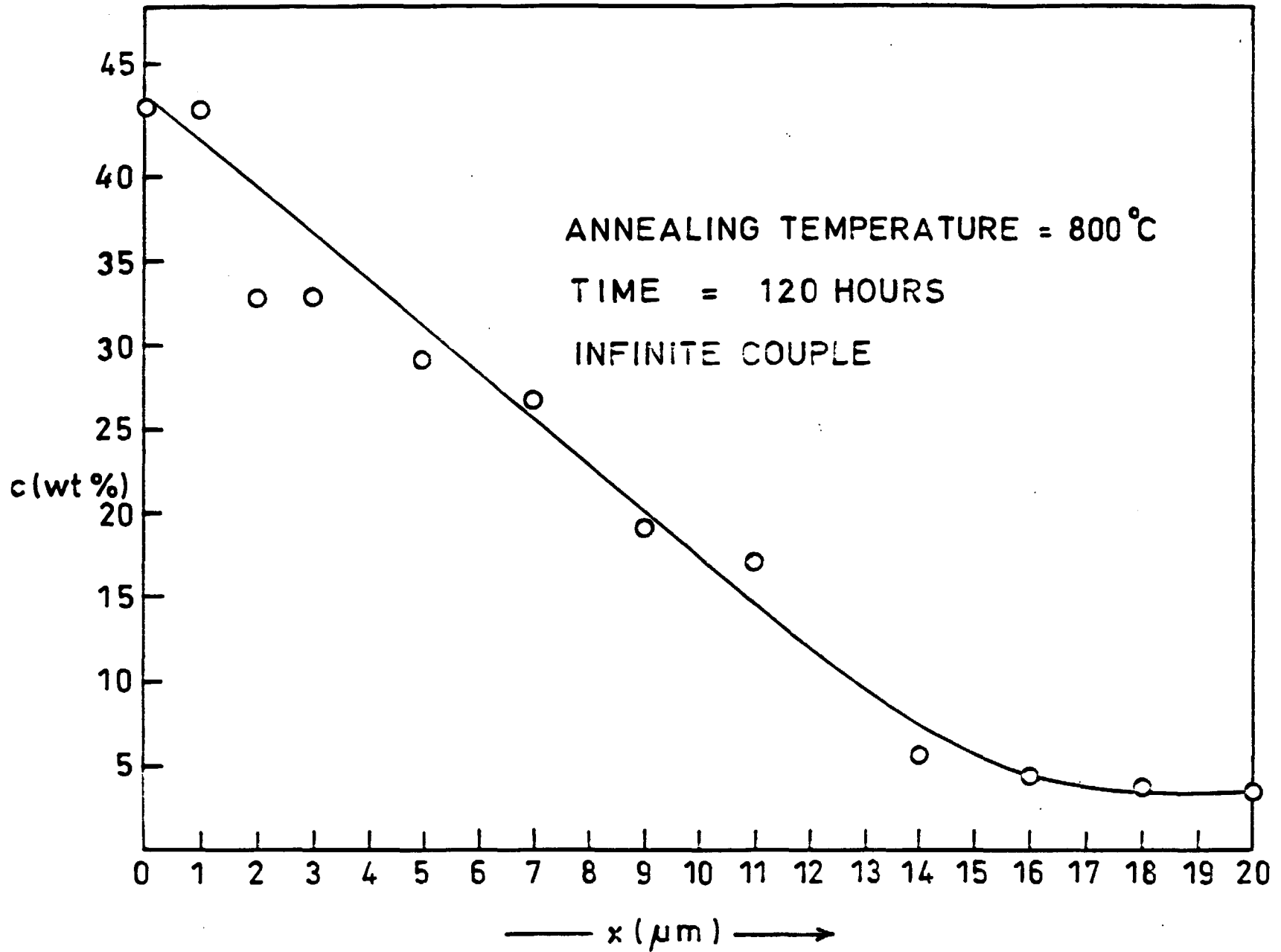


Fig.4

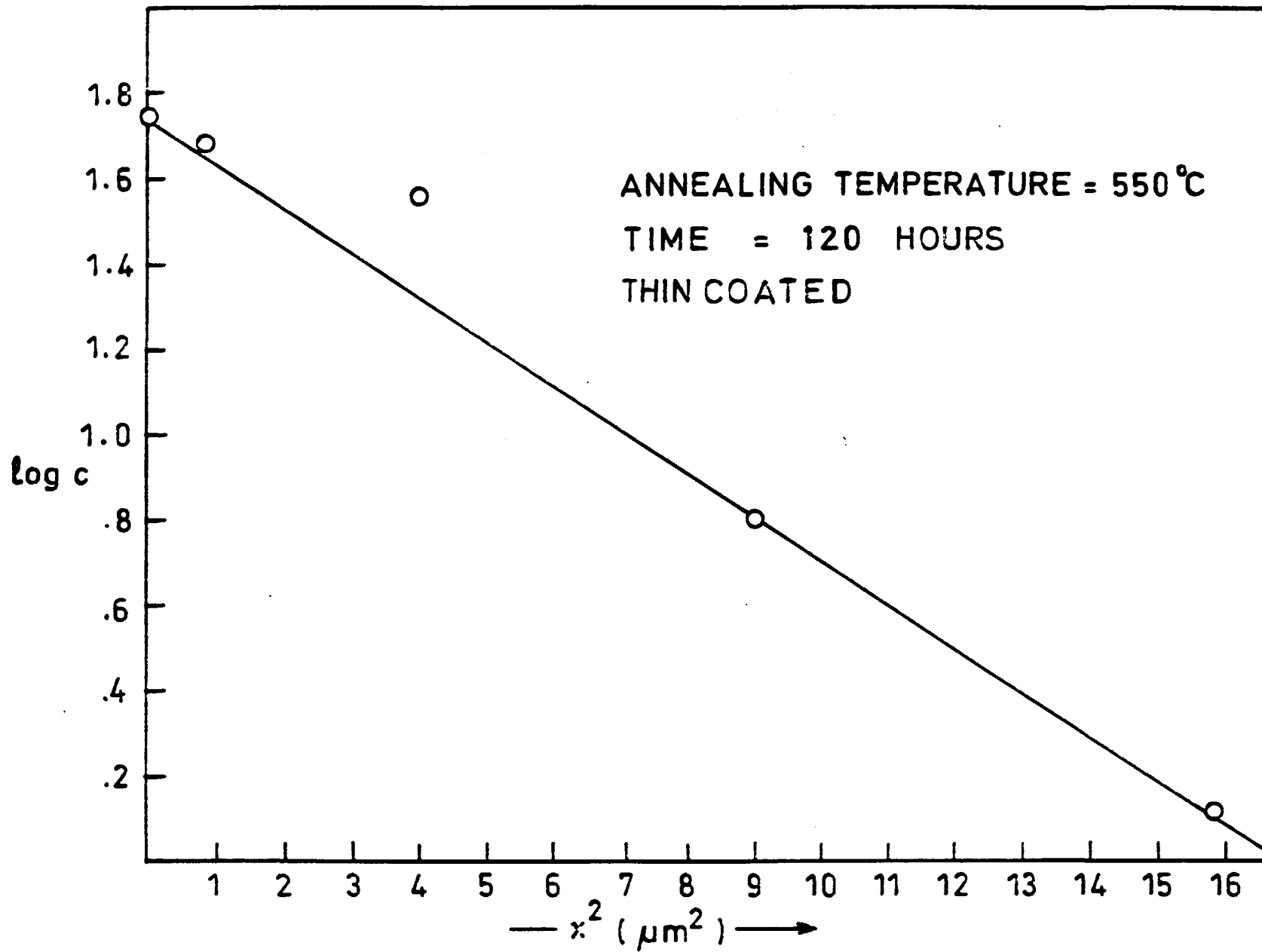


Fig. 5

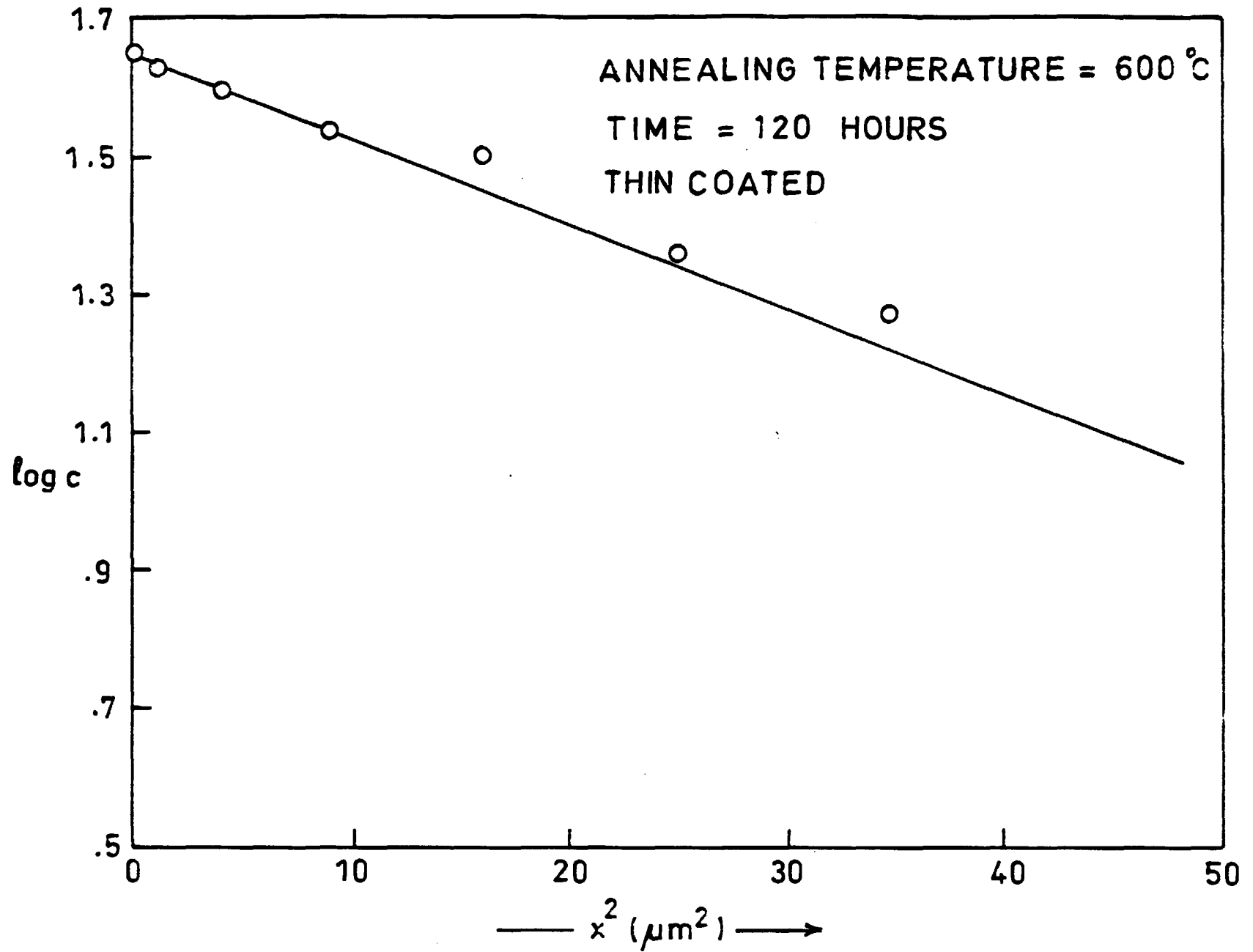


Fig.6

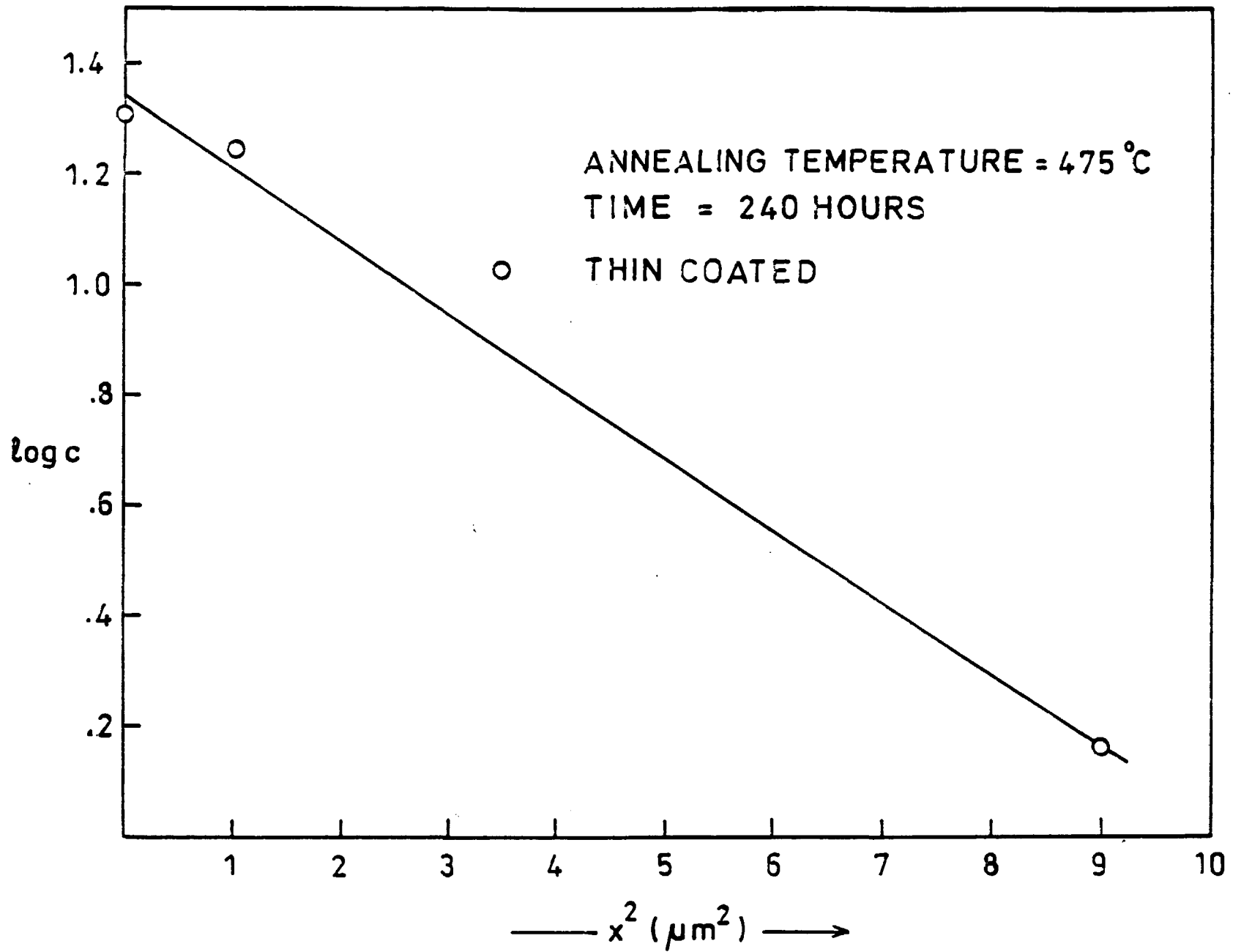


Fig.7

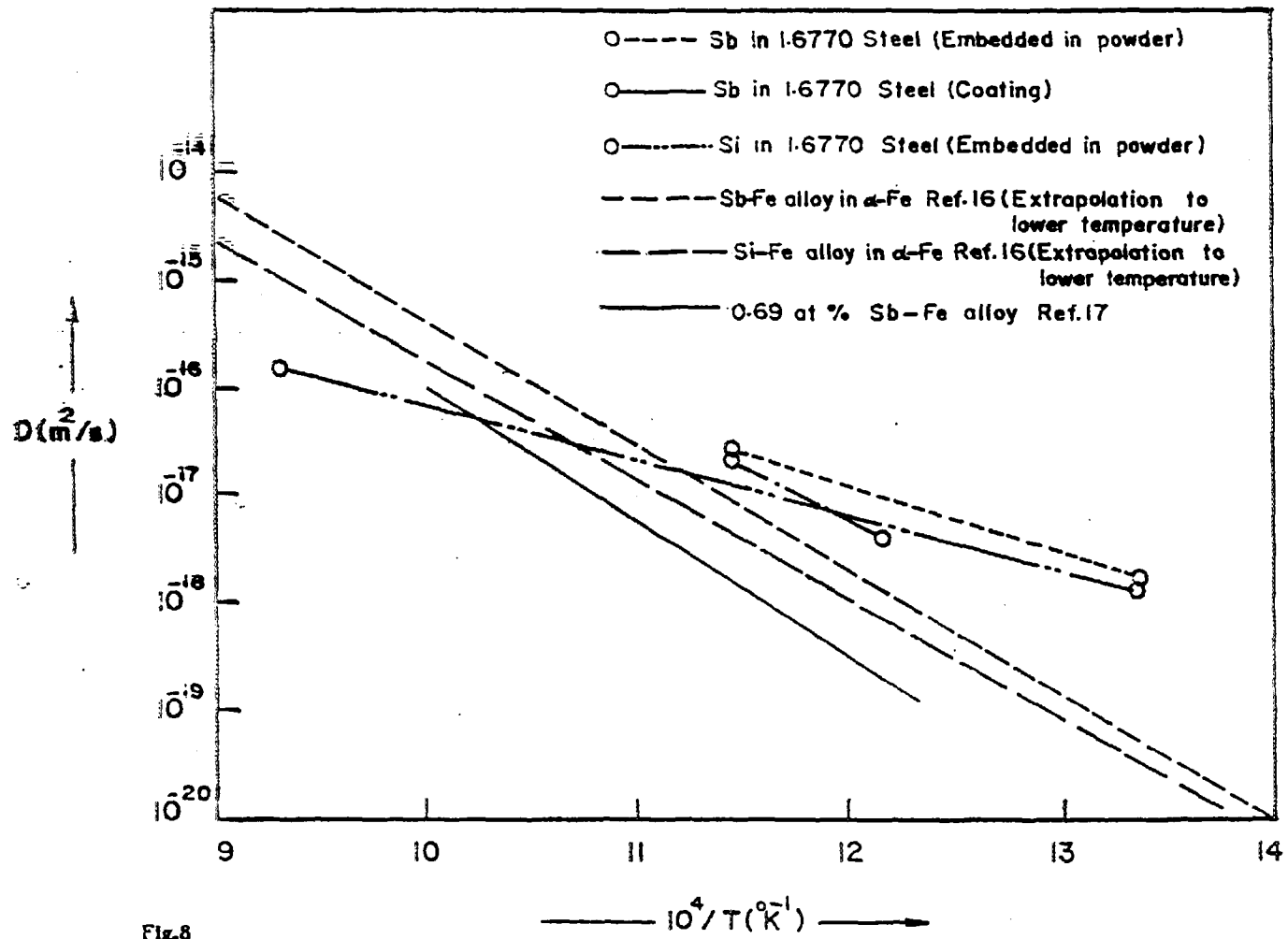


Fig.8