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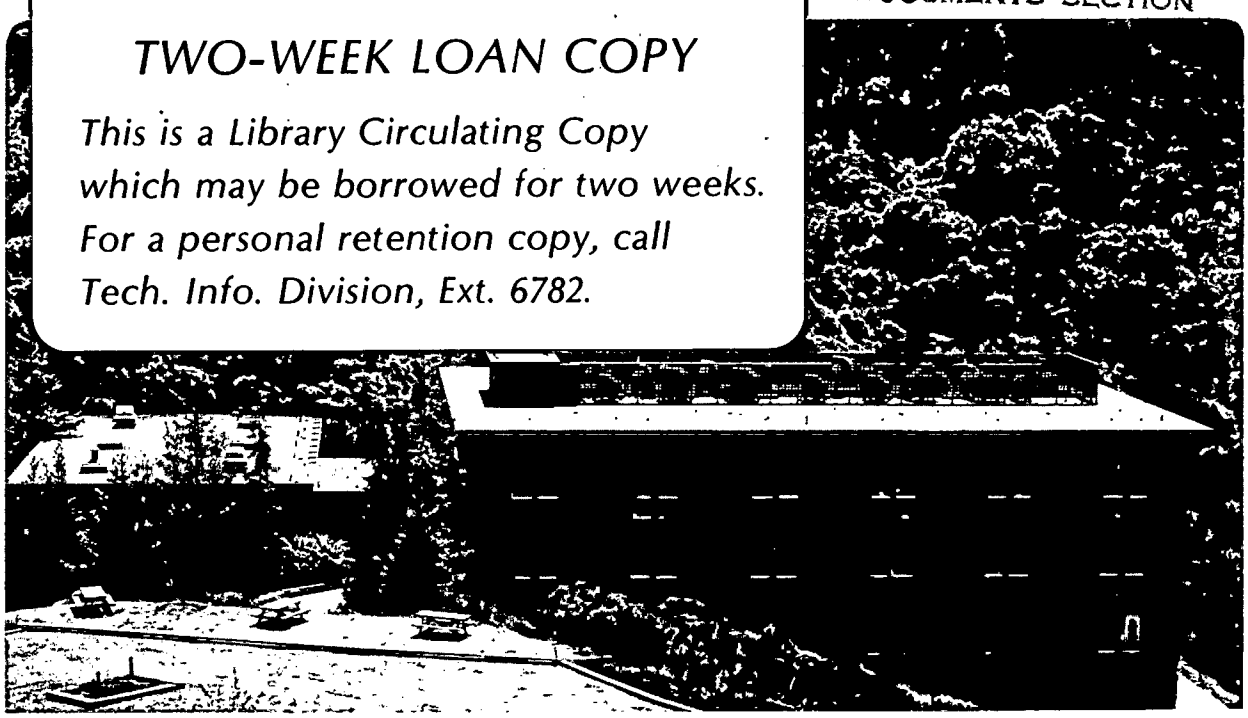

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CHEMICAL INTERDIFFUSION IN MULLITE

by

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ABSTRACT

A modified Boltzmann-Matano analysis of concentration profiles in mullite grown at the interface of a sapphire-fused silica diffusion couple in the range of 1678 to 1813°C indicates diffusivities of 5×10^{-12} to 10^{-10} cm^2/sec and the following chemical interdiffusion expression

$$\tilde{D} = 3.23 \times 10^{7} \exp\left[-(168 \pm 7 \text{ kcal/mol})/RT\right]$$

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*A portion of this work was conducted while the author was a Graduate Research Assistant at the University of California, Berkeley.

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I. INTRODUCTION

When a diffusion couple is annealed at a sufficiently high temperature, atom mobility is enhanced, and the components of the end phases interdiffuse to achieve a state of chemical equilibrium. The diffusion of the components is in such a direction as to eliminate any chemical potential gradient. At constant T and P, under equilibrium conditions, all the phase fields intersected by the corresponding isotherm and the isobar between the end phases will form as layers in the diffusion zone. Regardless of its thickness each phase must exist in the diffusion zone in order to provide a continuous and monotonic chemical potential gradient throughout the zone. If diffusion transport is the rate controlling mechanism, a local chemical equilibrium will exist at each interface. The resulting interfacial compositions thus correspond to either a liquidus or a solidus composition and can be used to construct the equilibrium phase diagram involving the end phases of the diffusion couple.

The above reasoning has culminated in recent investigations by Davis and Pask[1] and Aksay and Pask[2] concerned with the experimental determination of accurate stable and metastable phase equilibria and diffusion data in the SiO_2-Al_2O_3 system through the use of semi-infinite couples of various materials and the detection capabilities of the electron microprobe. The overall scope of this research also included the determination of the growth kinetics of the mullite solid solution at the interface of these couples.

II. EXPERIMENTAL

Mullite is the only stable intermediate phase in the Al_2O_3-SiO_2 diagram (Fig. 1). It is commonly described as having a composition of $3Al_2O_3 \cdot 2SiO_2$ but is, in fact, a solid solution whose equilibrium composition extends from 70.5 wt% to 74.0 wt% Al_2O_3. In the present research, diffusion couples composed of disks of (1) a 15 wt% Al_2O_3-85 wt% SiO_2 glass and sapphire or (2) fused SiO_2 and sapphire were heated for sufficient times to allow several microns of mullite growth at the interface (Fig. 2). Electron microprobe analysis revealed an Al_2O_3 composition range in the mullite layer from 70.5 wt% at the glass or SiO_2 interface to 74.0 wt% at the sapphire interface. Complete descriptions of the experimental procedures may be found in previous publications.[1-4]

III. RESULTS AND DISCUSSIONS

For the purpose of mathematical calculations, the diffusion couples following heat treatment may be described as a three phase system with two moving boundaries. A modified Boltzmann-Matano[5,6] analysis is applicable to this case in which a finite number of discontinuities occur in the concentration and the interdiffusion coefficient of one of the components throughout the total polyphase system. However, as shown by Gibbs[7], it is possible to describe the growth of the intermediate zone by regarding it as a homogeneous material with a concentration-independent chemical interdiffusion equal to

$$\tilde{D} = \frac{(\varepsilon'' - \varepsilon')^2}{4(\gamma_B - \gamma_A)^2 \, t} \qquad (1)$$

where ε'' and ε' are the positions of the interfaces between the end member

phases and the intermediate phase, γ_B and γ_A are constants and t is the time (Fig. 1). Microprobe analysis was conducted for both Al and Si. The concentration profiles of either Al or Si would be sufficient in the determination of $\tilde{D}$. Details of the mathematical procedures have been presented by Aksay[4].

As shown by Eq. (1), the determination of $\tilde{D}$ involves the visual determination of the thickness of the mullite layer as a function of time. The values for γ_A and γ_B were determined graphically knowing the values of the concentrations of the diffusing species at the interfaces. The values of these parameters for this research are presented in Table I.

The thickness of the mullite layer increased linearly with the square root of time, indicating that the growth mechanism is diffusion controlled. As noted above, the use of Eq. (1) assumes a concentration independent diffusivity for the diffusing component under study. The validity of this assumption was checked by the Boltzmann-Matano analysis of the Al concentration in the mullite layer grown at 1813°C; exactly the same diffusivity without concentration dependence was also obtained by this method. An Arrhenius plot of these diffusivities is shown in Fig. 3 and may be described by the expression

$$\tilde{D} = 3.23 \times 10^7 \exp\left[-(168 \pm 7 \text{ kcal/mol})/RT\right] \qquad (2)$$

The activation energy value is comparable to those determined in creep and hot pressing experiments on mullite by Hulse and Pask[8] (177 kcal/mol), Penty and Hasselman[9] (167 kcal/mol), Ghate et al[10] (163 kcal/mol) and Lessing et al[11] (164 kcal/mol). The values of the stress exponents in the creep experiments varied between 1.0 and 1.4 which is a strong indication of a creep process controlled by a diffusional mechanism, i.e. either Coble (grain-

boundary diffusion) or Nabarro-Herring (bulk diffusion). In this study $\tilde{D}$ corresponds to bulk diffusion since the mullite formed as single crystal layers. This would indicate that the creep mechanism is controlled by the bulk diffusion and is probably a Nabarro-Herring process.

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Table I. Experimental conditions and necessary data for the calculation of $\tilde{D}$ in mullite.

Temp. IPTS-68 (°C)	(sec x 10^{-5})	Mullite Thickness (μm)	γ_A	γ_B	Diffusivity, $\tilde{D}$ (cm^2/sec)
1678*	7.309	10.00	-0.140	0.112	5.39×10^{-12}
1678*	28.428	18.00	-0.140	0.112	4.49×10^{-12}
1703	3.456	8.53	-0.140	0.115	8.10×10^{-12}
1703	6.048	11.30	-0.140	0.115	8.10×10^{-12}
1703	7.776	13.35	-0.140	0.115	8.12×10^{-12}
1703	9.504	15.10	-0.140	0.115	8.82×10^{-12}
1703	9.504	15.10	-0.140	0.115	9.23×10^{-12}
1753*	3.965	13.00	-0.135	0.126	1.56×10^{-11}
1813*	6.015	36.00	-0.135	0.130	9.76×10^{-11}

*Equilibrium liquid compositions. All the other runs employed a non-equilibrium melt composition of 15.0 wt% Al_2O_3.

FIGURE CAPTIONS

Fig. 1. The relationship between the concentration profile of a semi-infinite SiO_2-Al_2O_3 diffusion couple and the phase diagram, at temperature T below the melting point of mullite. Boltzmann-Matano interface corresponds to the phase boundary at t = o.

Fig. 2. Interference-contrast micrographs of the diffusion zone between a couple of sapphire and (A) 10.9 wt% Al_2O_3 containing silicate at 1678°C for 7.309×10^5 sec (1.72.1); (B) 22.8 wt% Al_2O_3 containing silicate at 1753°C for 3.965×10^5 sec (2.72.1A), and (C) 42.2 wt% Al_2O_3 containing silicate at 1813°C for 6.015×10^5 sec (1.72.2A). The prismatic precipitates in the top portion of the diffusion zone in the silicate are mullite that crystallized during cooling.

Fig. 3. Arrhenius plot of diffusivity vs reciprocal of absolute temperature for diffusion in mullite.

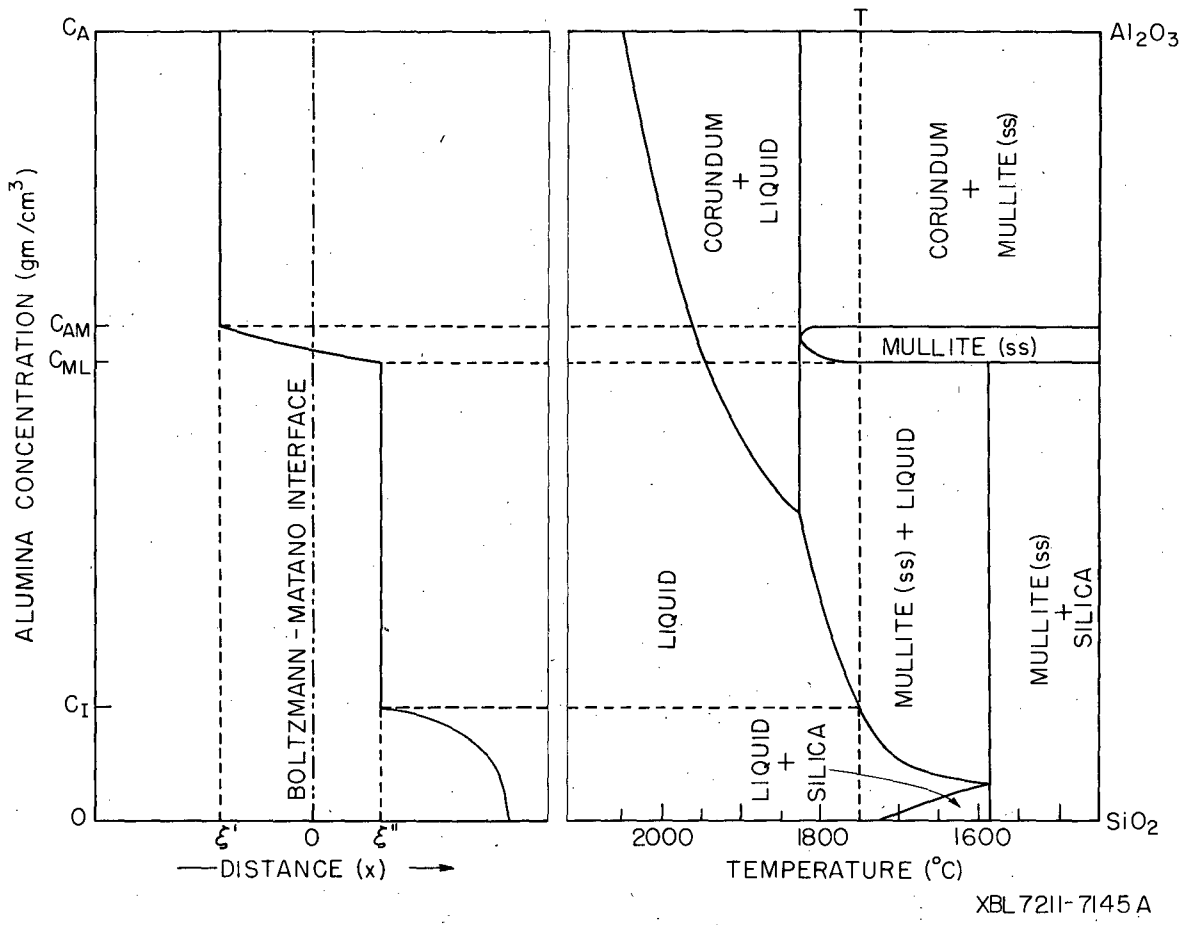
ALUMINA CONCENTRATION (gm/cm³)
C_A
C_AM
C_ML
C_I
0
BOLTZMANN-MATANO INTERFACE
ξ'
0
ξ''
DISTANCE (x)
T
Al2O3
SiO2
CORUNDUM + LIQUID
CORUNDUM + MULLITE (ss)
MULLITE (ss)
LIQUID
MULLITE (ss) + LIQUID
MULLITE (ss) + SILICA
LIQUID + SILICA
2000
1800
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Fig. 1

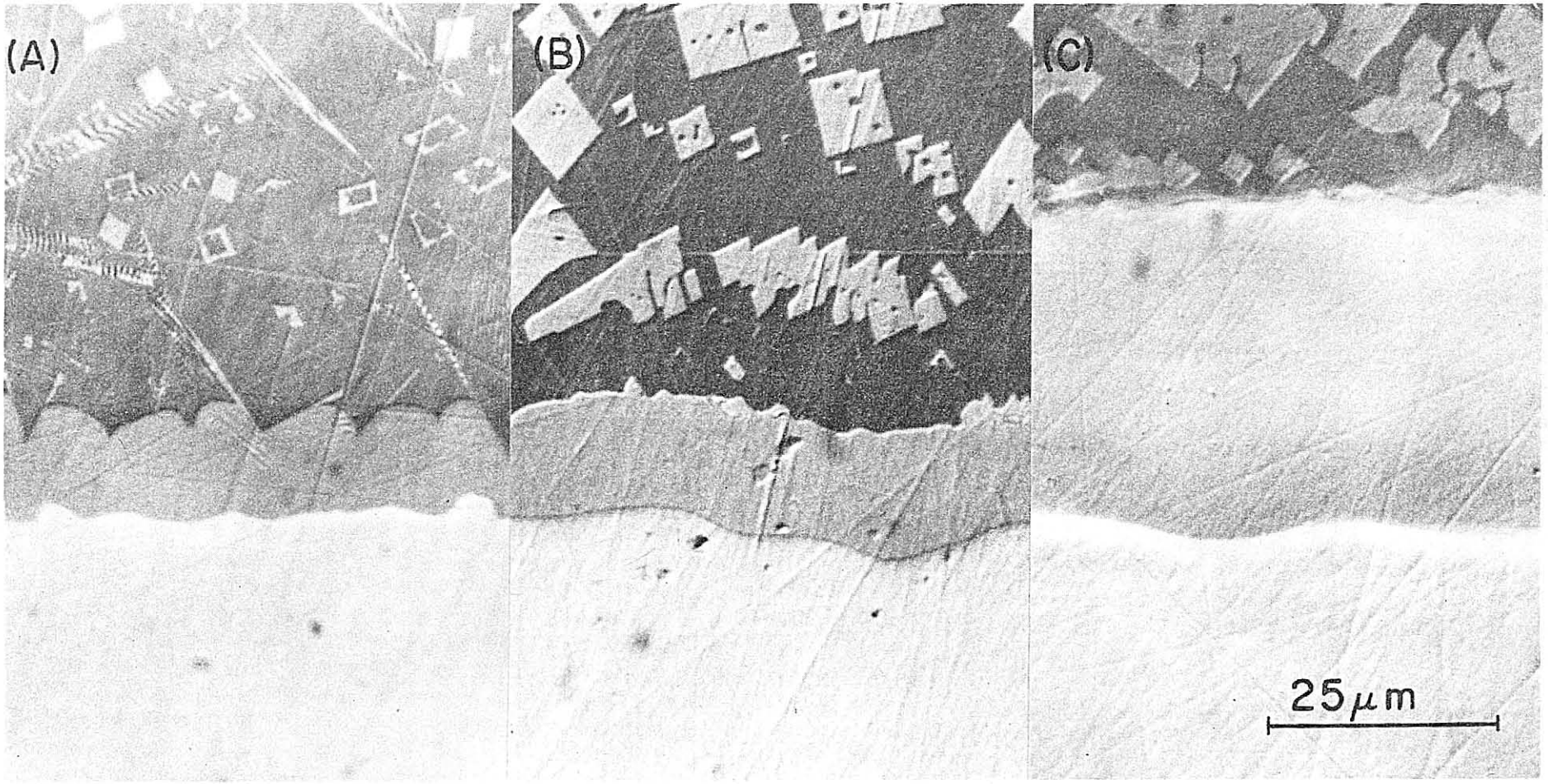

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Fig. 2

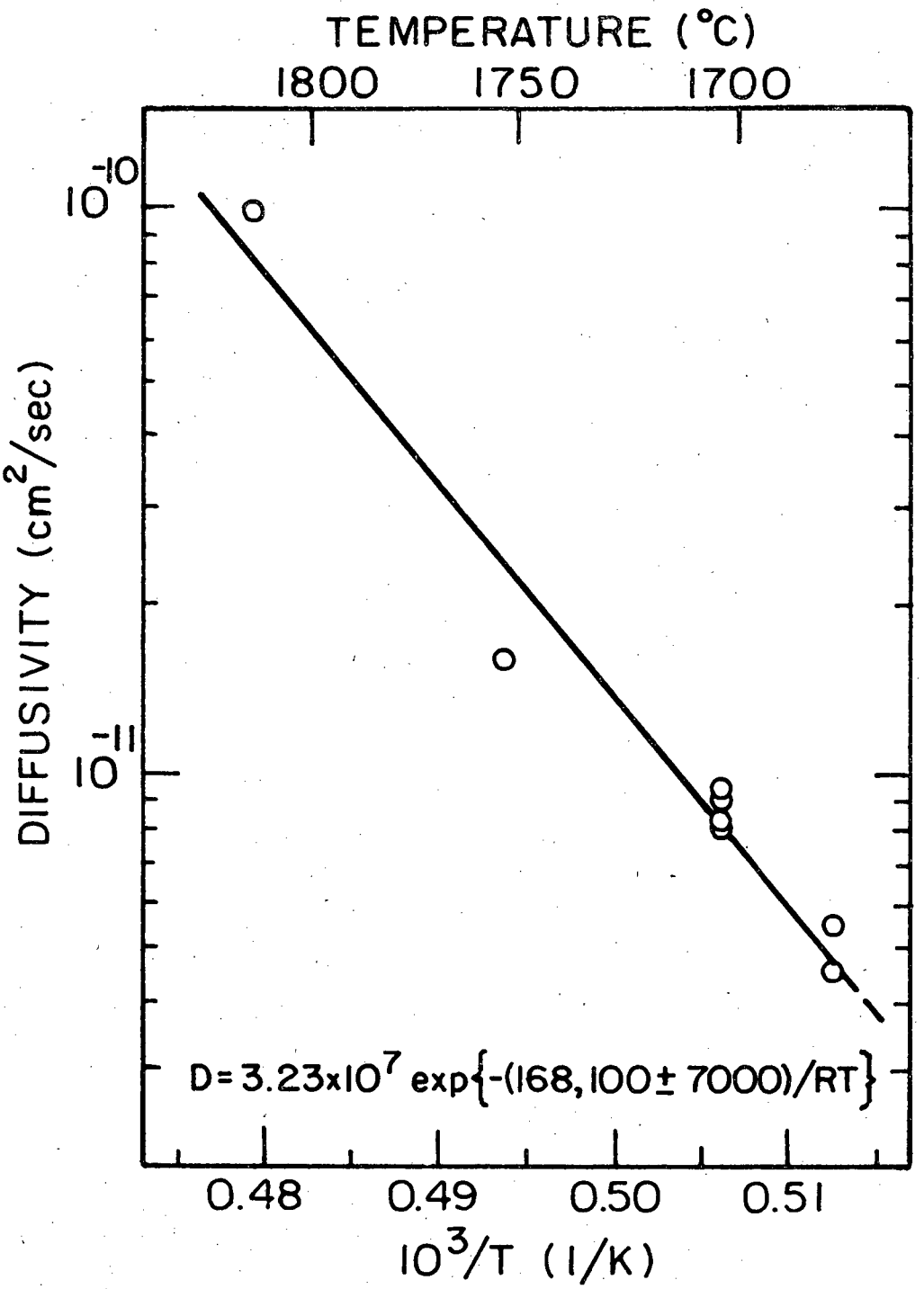

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Fig. 3

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